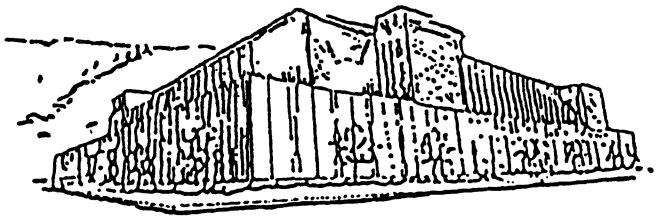
1995

Assessing the cosolvent effects of ethylene glycol, aqueous ammonia, and acetone on the sorption and mobility of tetrachloroethylene in soil

Lisa Selina Ivanich
The University of Montana



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Date July 25, 1995

ASSESSING THE COSOLVENT EFFECTS OF ETHYLENE GLYCOL, AQUEOUS AMMONIA, AND ACETONE ON THE SORPTION AND MOBILITY OF TETRACHLOROETHYLENE IN SOIL

by

LISA SELINA IVANICH

B.S., Montana College of Mineral Science and Technology, Butte, 1993

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Assessing the Cosolvent Effects of Ethylene Glycol, Aqueous Ammonia, and Acetone on the Sorption and Mobility of Tetrachloroethylene In Soil

Advisor: Dr. Garon C. Smith GCS

A number of chlorinated organic compounds including tetrachloroethylene (PCE) are listed as EPA priority pollutants. They are toxic and carcinogenic, posing a serious health threat at concentrations as small as the part per billion range. PCE is commonly used as a solvent, degreasing agent, intermediate in chemical synthesis, and in household items such as cleaners, paints, and polishes. Prevalent use and improper disposal directly affects communities through the contamination of ground water supplies. Cosolvency poses as an extra complication to greatly accelerate the movement of chlorinated hydrocarbon contaminents into ground water. Cosolvency occurs when a polar organic solvent comes in contact with contaminents bound in soil and promotes their solubility into the ground water.

This study investigates the cosolvency effects of three solvents - anti-freeze, acetone, and aqueous ammonia, on the sorption and mobility of tetrachloroethylene within a soil matrix.

Soil samples were collected from the construction site of the Gallagher Business building on campus at the University of Montana. The soil was sequentially sieved, and grain-size distributions determined. Soils with a symmetric particle distribution were found most suitable for column flow characteristics. Soil slurries in deionized water were packed into a glass column (Pharmacia) in which a dynamic 1.5 ml/min flow of water was established via a hydraulic head resevoir. Sixteen 35 ml water fractions from the column were collected for each experiment. PCE (6μl) was injected at the beginning of collecting fraction two and 6 ml of the cosolvent were injected at the beginning of fraction nine. The fractions were extracted with methyl tertiary butyl ether (MTBE) and analyzed with a Gas Chromatograph/Mass Spectrometer to monitor the PCE concentration in each fraction. Elution profiles show PCE emerging from the column and dropping asymptotically. A dramatic increase in PCE concentration occurred after the cosolvent was introduced to the system. Each cosolvent raised the eluent PCE concentrations by greater than an order of magnitude - anti-freeze (13.4), acetone (12.0), and aqueous ammonia (17.1).

Results of this study demonstrate that the disposal of cosolvents such as antifreeze, acetone, and aqueous ammonia in drains may exacerbate transport and miscibility of PCE into the public drinking water supply. Therefore, cosolvency is an important factor to consider when determining the fate and transport of PCE and other chlorinated organic contaminants in the environment.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION AND STATEMENT OF THE PROBLEM

Halogenated solvents are ubiquitous contaminants in urban water supplies. Chlorinated aliphatic hydrocarbons are commonly used as solvents, degreasing agents, intermediates in chemical syntheses, and in household items such as cosmetics, cleaners, laundry products, paints, polishes, and preservatives. A number of halogenated organic compounds such as trichloroethylene, tetrachloroethylene, dichloromethane, and chloroform are found on EPA's list of 129 priority pollutants because they are toxic, carcinogenic, and pose a serious health threat at concentrations as small as the part per billion range *(1)*. The most likely source of ground water contamination from halogenated solvents is improper disposal of contaminated wastes by dry cleaners, machine shops, dental tool manufacturers, and automotive repair facilities. Prevalent use and uncontrolled disposal directly affects us through the contamination of ground water supplies in many communities including the Missoula Valley Aquifer.

In 1988, detectable quantities of chlorinated organic compounds including tetrachloroethylene, 1,1,1-trichloroethane, and dibromochloromethane were discovered when Mountain Water Company began sampling wells in Missoula. The Missoula Valley Aquifer provides water to over 80% of the county's 78,000 residents. As a first step to protect the ground water from further contamination, the Missoula Valley Aquifer was designated as the first federally "sole source aquifer" in the summer of 1988 (*2*). Shortly thereafter, a systematic investigation of the extent of solvent contamination was initiated.

SOURCES OF CHLORINATED SOLVENTS IN THE MISSOULA VALLEY AQUIFER

Once the presence of chlorinated hydrocarbons in Missoula's ground water was confirmed, potential sources of contamination needed to be determined. Sampling sites were selected by finding businesses that were "probable" users of products containing halogenated solvents -- automotive repair facilities, dry cleaning agencies, and car washes. The results of the survey are depicted graphically in figures that follow. The right side of each figure enumerates the common contaminants that were anticipated to be present. Note that only compounds numbered 1 through 15 refer to chlorinated species

Since samples collected by the Missoula City-County Health Department revealed that tetrachloroethylene (PCE) was the most common chlorinated contaminant in its well samples, its prominence was anticipated. This is borne out by the survey. The highest detectable levels of PCE were found in sludge samples at a local tire/vehicle maintenance shop (Figure 1-1). PCE is an ingredient in carburetor cleaners and cleaning solvents used by the automotive repair businesses which extensively employed floor drains (EPA's Class V injection wells); hence, the most common route of contamination was determined to be sumps used in and around automotive shops ***(2)***.

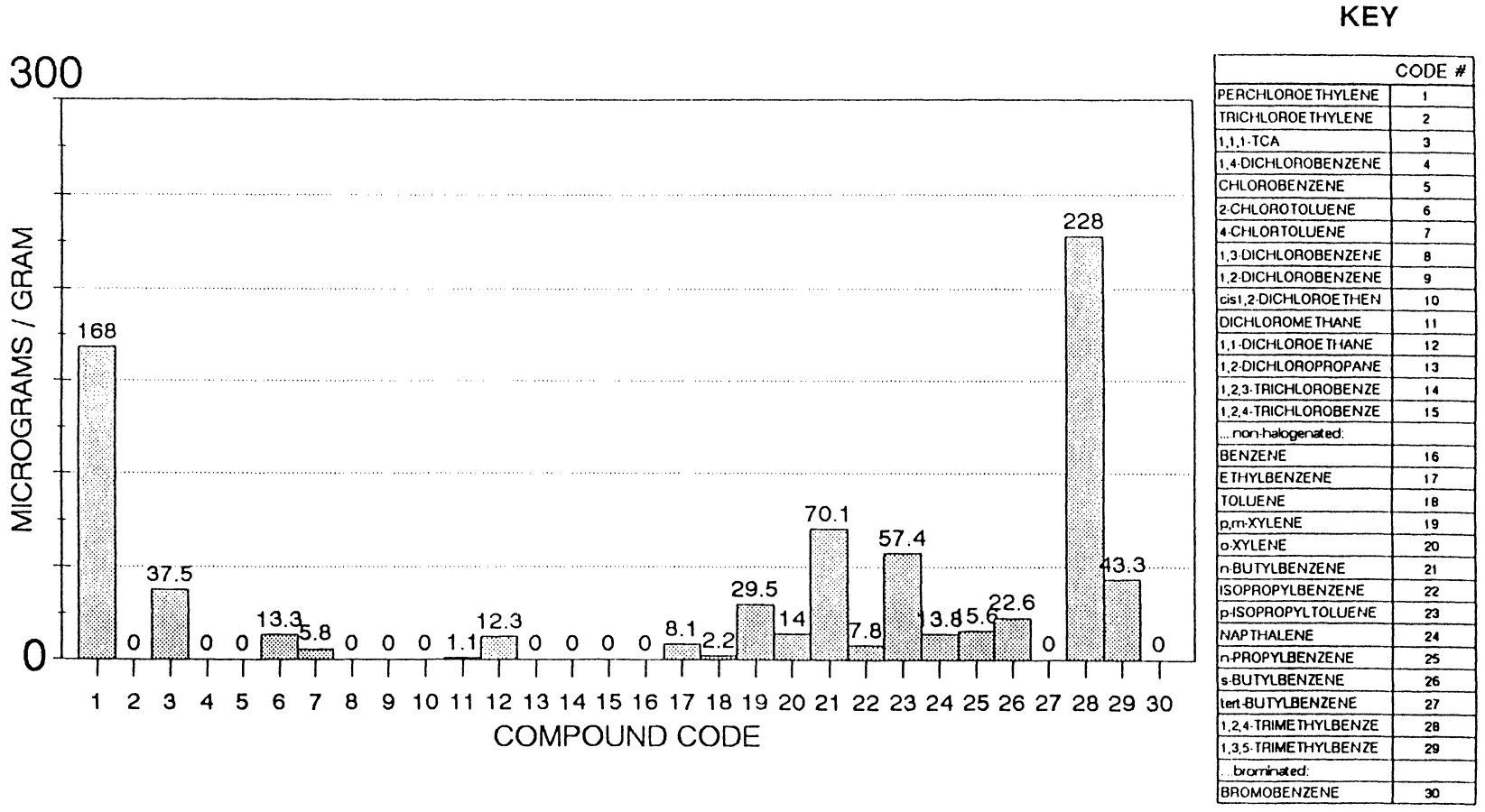


Figure 1-1. PCE Detection. Levels of chlorinated compounds found in sludge at a local tire/vehicle maintenance shop. Note the levels of tetrachloroethylene. (Taken from English, 1991, Appendix A.)

Dry cleaners, which use large quantities of PCE, had only small detectable levels (Figure 1-2). Dry cleaning agencies are considered past sources of chlorinated organic compound contamination. Currently, they use a combination of closed systems to recycle their PCE and air strippers to remove it from plant wastewater. No other chlorinated contaminants were discovered in dry cleaning establishments.

The lowest levels of chlorinated contaminants were observed for car washes (Figure 1-3), with no detectable levels of PCE.

PCE contamination represents a serious regulatory liability for automotive shops and dry cleaners. That tetrachloroethylene was present in the injection well sludge of automotive repair sites suggests liquid wastes containing it were flushed down the drain. This could easily contaminate a large volume of ground water for which the allowable Maximum Concentration Limit of PCE is 5 μg/L (5 ppb). Sludge from the bottom of solvent recycling stills was found on the ground outside one dry cleaner. It displayed an unbelievably high PCE level of 12,622 μg/g, i.e., 1.2%!

SORPTION AND MOBILITY OF RELEASED CONTAMINANTS

Protection of an aquifer from contamination by halogenated solvents relies on an understanding of factors that promote their transport into an aqueous medium. When

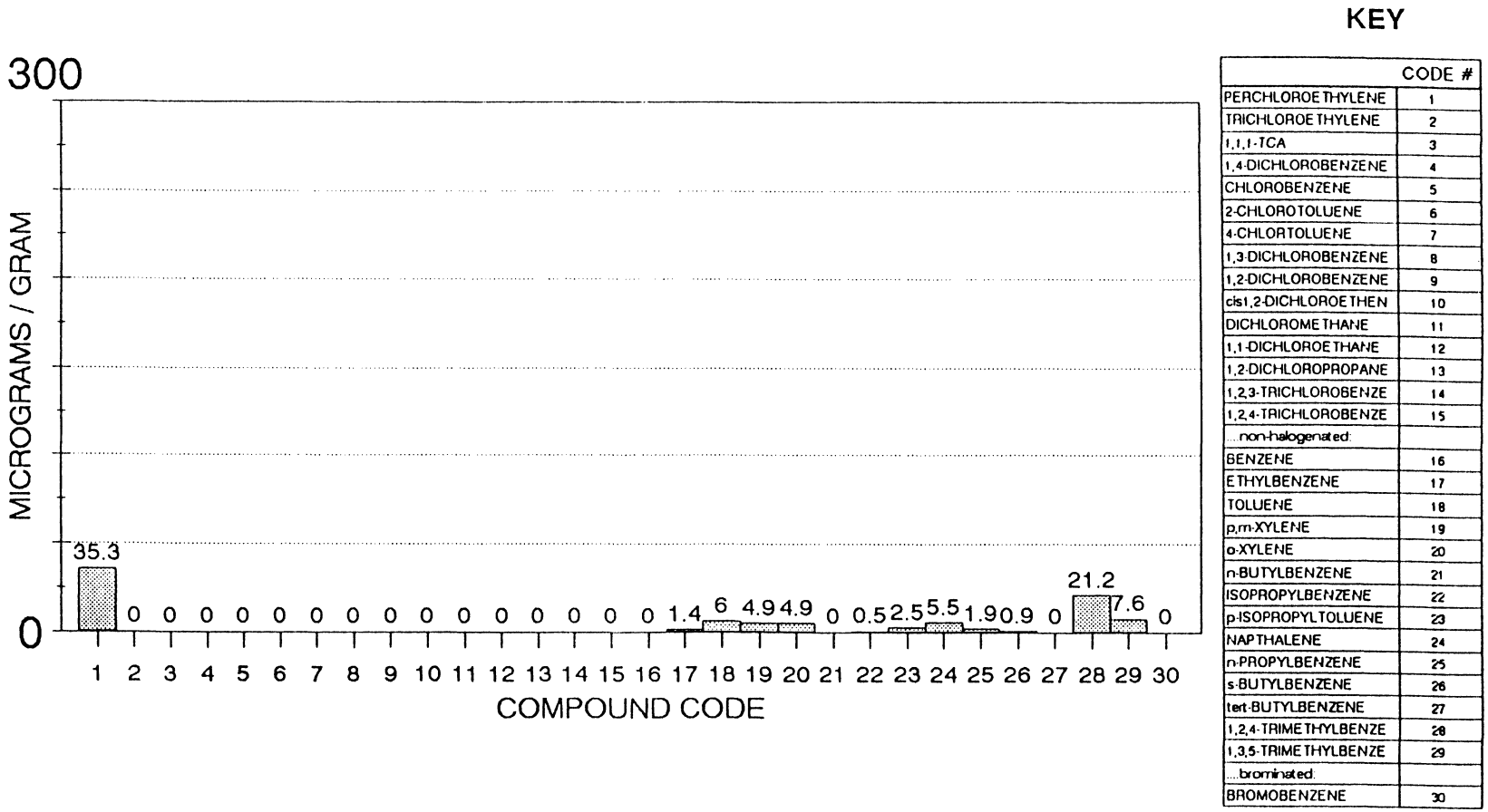
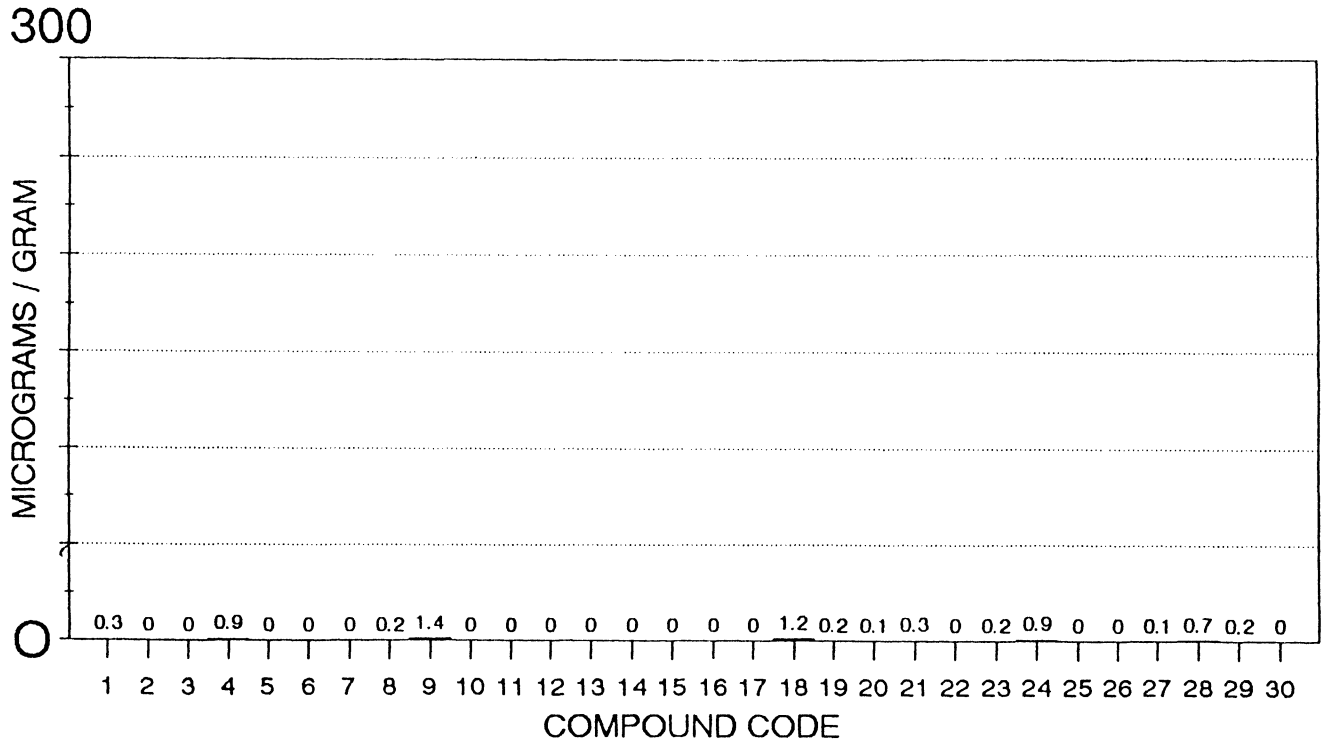


Figure 1-2. PCE Detection. Levels of chlorinated hydrocarbons taken from soil at a local dry cleaning agency. Tetrachloroethylene was present at a small detectable level. (Taken from English, 1991, Appendix A.)



KEY

	CODE #
PERCHLOROETHYLENE	1
TRICHLOROETHYLENE	2
1,1,1-TCA	3
1,4-DICHLOROBENZENE	4
CHLOROBENZENE	5
2-CHLOROTOLUENE	6
4-CHLORTOLUENE	7
1,3-DICHLOROBENZENE	8
1,2-DICHLOROBENZENE	9
cis1,2-DICHLOROETHEN	10
DICHLOROMETHANE	11
1,1-DICHLOROETHANE	12
1,2-DICHLOROPROPANE	13
1,2,3-TRICHLOROBENZE	14
1,2,4-TRICHLOROBENZE	15
....non-halogenated:	
BENZENE	16
ETHYLBENZENE	17
TOLUENE	18
p,m-XYLENE	19
o-XYLENE	20
n-BUTYLBENZENE	21
ISOPROPYLBENZENE	22
p-ISOPROPYLTOLUENE	23
NAPTHALENE	24
n-PROPYLBENZENE	25
s-BUTYLBENZENE	26
tert-BUTYLBENZENE	27
1,2,4-TRIMETHYLBENZE	28
1,3,5-TRIMETHYLBENZE	29
....brominated:	
BROMOBENZENE	30

Figure 1-3. PCE Detection. Low levels of chlorinated hydrocarbons present in sludge samples taken from a local car wash. There was no detectable level of tetrachloroethylene. (Taken from English, 1991, Appendix A.)

assessing the likely environmental fate of chlorinated organic compounds, their sorption and solubility characteristics are the principal controlling factors. Tetrachloroethylene and other chlorine-containing compounds are hydrophobic in nature. These chemicals, then, have an affinity to become trapped in pore spaces of sludge and fine soils. They remain in place until a hydraulic head forces the organic compounds out of the pores and deeper into the water table, or until they dissolve into an aqueous mobile phase*(2)*.

Degradation of subsurface PCE is very slow*(2)*. With a density of 1.63 g/ml, tetrachloroethylene, (C_2Cl_4) is heavier than water. Once it enters the water table, it will sink to the bottom of an aquifer as a DNAPL (dense non-aqueous phase liquid). The strong C-Cl bonds are not easily metabolized by microbes nor do they abiotically weather. This gives PCE the ability to remain in ground water and dissolve slowly, causing significant contamination over the long term *(2)*.

An extra complication can arise to greatly accelerate the movement of chlorinated hydrocarbon contaminants into the ground water. Accidental spills or improper disposal of polar compounds (e.g., anti-freeze, ammonia, acetone) can come in contact with the soil-bound organic compound(s), and promote their solubility into ground water. This thesis explores situations in which soil-bound PCE, the most prevalent chlorinated contaminant in Missoula, is exposed to "releases" of nonaqueous compounds that become a cosolvent with water.

Cosolvency, as defined by Pinal *et al.* ***(3)***, refers to the increased solubility of hydrophobic organic contaminants in the presence of completely miscible organic solvents (CMOS) and/or partially miscible organic solvents (PMOS). According to Yalkowsky *et al.* ***(4)***, polar organic molecules become bridging solvent molecules when present in a relatively large abundance (more than 10% by volume where there is insufficient water to hydrate most of them). They can partially surround a chlorinated organic compound, approximately in proportion to their volume ratio in the solution, enhancing the solubility of the hydrophobic chlorinated hydrocarbon (Figure 1-4).

When the cosolvent comprises more than 10% of the solution volume, a distinct change in the activity coefficients of nonpolar chemicals occurs which is an important factor influencing the fate of these organic chemicals in the environment ***(5)***. Table 1-1 shows the solubility enhancement observed for pyrene, a four-ring aromatic hydrocarbon, in the presence of water and nine commonly encountered polar organic solvents.

SIGNIFICANCE OF THIS RESEARCH

This research was proposed to demonstrate the health risks imposed by irresponsible or accidental releases of cosolvents in systems that have also received chlorine-containing compounds. It underscores the need for public education that disposal of products such as antifreeze in drains exacerbates transport and mobility of toxic substances into public drinking water supplies.

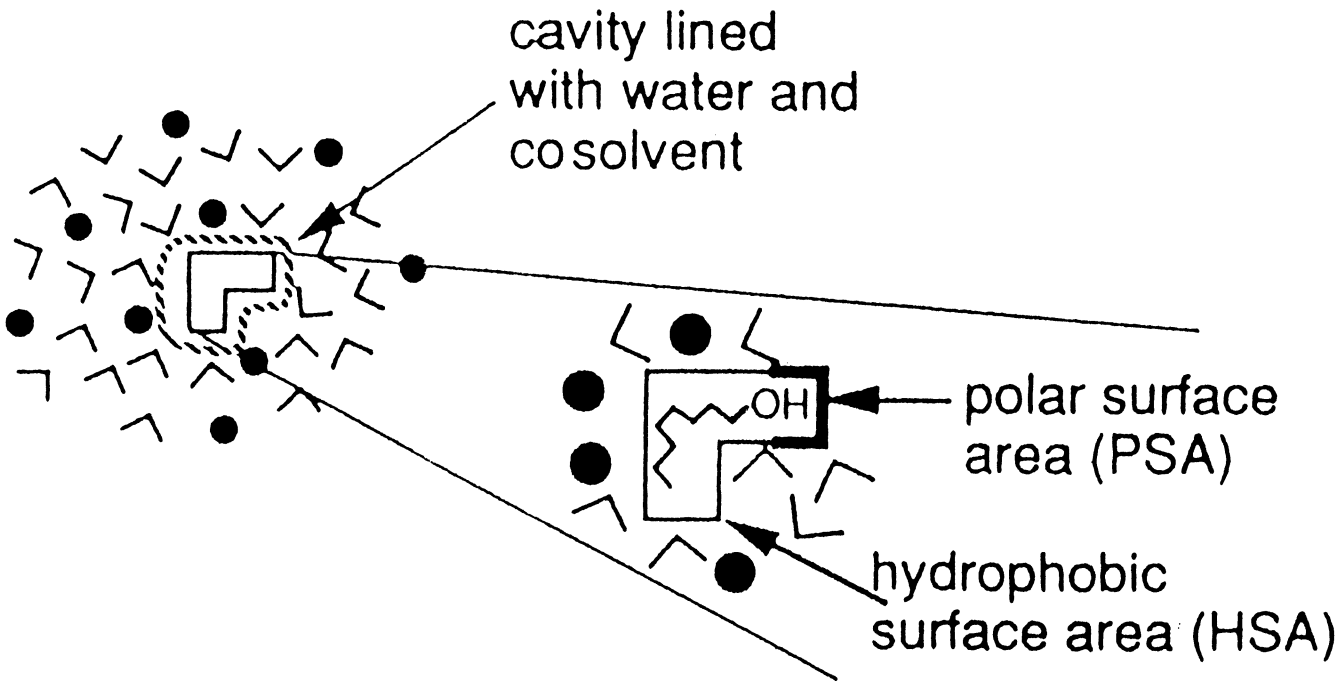


Figure 1-4. Cosolvency. Other dissolved organic substances (●) affect the water molecules surrounding an organic compound of interest (╔). (From Schwarzenbach, *et al.*, 1993, p.99)

Table 1-1. Estimated Solubility Enhancement of Pyrene.
(From Schwarzenbach *et al.*, 1993, p.101)

	Cosolvent	**Enhanced Solubility**	
		Yalkowsky	Morris
1.	Water	1	
2.	Glycerine	1.6	
3.	Formamide	1.7	
4.	Ethylene Glycol	2.3	1.9
5.	Propylene Glycol	2.8	2.5
6.	Isopropanol	3.3	3.9
7.	Methanol	3.9	2.8
8.	Ethanol	3.9	3.3
9.	Acetonitrile	3.9	3.6
10.	Acetone	3.9	3.6

These experiments represent what we believe are the first attempt to explore the competition between cosolvency and sorption during a "pulse" release of cosolvent, a realistic scenario that can be expected to frequently occur in urban settings. The experimental results provide quantitative determinations to employ in transport modelling and risk assessment calculations.

This research has particular significance to the Missoula community. On September 8, 1994, the Missoula Valley Water Quality District (part of the Environmental Health Division of the Missoula City-County Health Department) enacted an Aquifer Protection ordinance to help protect Missoula's sole source drinking water supply. The ordinance contains a provision banning the use of tetrachloroethylene except for dry cleaners and educational labs. EPA has ordered the elimination of Class V injection wells suggesting alternatives for proper disposal of the wastes from the automotive repair facilities which include installation of a holding tank or operation of a dry shop. The findings presented in this study constitute a dramatic example of cosolvency to use in educational programs in Missoula and other communities with unconfined aquifer, drinking water supplies.

THESIS ORGANIZATION

The organized outline for the remainder of this thesis is given below:

CHAPTER 2: Review of the scientific literature: studies of cosolvent effects.

CHAPTER 3: Description of the methods employed in this project, sample collection, storage, extraction, and instrumentation.

CHAPTER 4: Soil description and characterization.

CHAPTER 5: Cosolvency

CHAPTER 6: Discussion and Conclusion.

CHAPTER 2

LITERATURE REVIEW OF COSOLVENCY STUDIES

Research on cosolvency first appeared in the pharmaceutical literature around 1953 (e.g., Higuchi et al., 1953; Peterson and Hopponen, 1953). A firm theoretical treatment of the phenomenon is attributed to Yalkowsky and co-workers *(4)*. They focused on how inclusion of polar organic compounds as cosolvents significantly impacted the solubility of organic drugs in aqueous systems. After examining six organic cosolvents, they concluded that the logarithm of a hydrophobic compound's solubility was directly related to the fraction of cosolvent present. The general form of their relationship that expresses the observed solubility enhancement due to cosolvency is:

$$\log\left(\frac{C_{mix}^{sat}}{C_{w}^{sat}}\right) = \frac{0.5\left(\sigma_{t:w} - \sigma_{t:c}\right)\left(N \cdot \mathrm{HSA} \cdot f_{c}\right)}{2.303RT} \qquad \textbf{(2 - 1)}$$

where C represents the equilibrium concentration (moles/L) of the organic substance in water (w) or the cosolvent-water mixture (mix);

σ is the interfacial surface energy (erg/cm^2) between tetradecane (t) and water (w) or cosolvent (c);

N is Avogadros number;

HSA is the hydrophobic surface area of the organic solute in cm^2/molecule;

f_c is the volume fraction of cosolvent in the mixture;

R is the gas constant; and

T is the solution temperature in Kelvin

Rao and co-workers applied Yalkowsky's equations to mobility studies of organic contaminants in the environment beginning in 1985 (e.g., ***(6)***, ***(7)***, ***(8)***, and ***(9)***). They documented the influence of completely miscible organic cosolvents on sorption and transport of hydrophobic organic compounds in soils. The outcome of their work was the Solvophobic Theory, an equation to characterize the exponential decrease in sorption coefficient (K_m) as the fraction of the organic cosolvent in binary solvent mixtures increases:

$$\ln(K_m / K_w) = -\alpha\ \sigma_c f_c \qquad \textbf{(2 - 2)}$$

where α is the empirical portion of the slope from the ln K vs. f plot; and

σ is the remainder of the slope attributable to interfacial surface tension and surface.

Pinal and co-workers ***(3)*** investigated the solubility of hydrophobic organic contaminants in complex mixtures, emphasizing the impact of the presence of PMOS as cosolvents. From their research, they were able to conclude that a partially miscible organic solvent may be classified into one of two broad groups: 1) conditional or nonpolar

groups: 1) conditional or nonpolar solvents, characterized by low aqueous solubility and only minor effects on HOC solubility; and 2) unconditional or polar solvents, which had large aqueous solubilities and increased HOC solubility considerably.

Using Rao's Solvophobic Theory, Nkedi-Kizza and co-workers ***(7)*** were able to successfully interpret a series of batch sorption experiments. They measured the sorption of anthracene and two herbicides, diuron and atrazine, by soils from binary solvent mixtures of methanol-water and acetone-water solutions. Results from this "batch slurry method" with five different soils complied with the theory.

A second study, done by Nkedi-Kizza *et al.* ***(10)*** used air-dried Eustis soil packed into a glass preparative-scale, high-performance liquid chromatography column to measure the sorption and leaching behavior of diuron and atrazine by eluting the column with water and solutions of methanol-water. Again, the results showed that increasing the fraction of organic cosolvent resulted in an exponential decrease in sorption which, in turn, led to an enhanced pesticide mobility through the soil.

Walters and Guiseppi-Elle ***(11)*** examined the ability of Solvophobic Theory to explain experimental data for sorption of dibenzodioxins by soils when binary mixed solvents are present. Their samples were collected from the Times Beach, MO Superfund site.

In addition to cosolvency studies, research has been conducted concerning transformation, desorption, and adsorption of halogenated organics - specifically tetrachloroethylene with various soils and sediments. The behavior of PCE is important to understand with respect to a cosolvency study.

In a study by Schreirer and Reinhard, tetrachloroethylene present in landfill leachate underwent transformation into trichloroethylene, ethene, and ethane by iron powder *(22).*

Using batch experiments, Farrell and Reinhard examined sorption mechanisms affecting isotherm shape of tetrachloroethylene. The results of their study indicated that adsorption in micropores contributes significantly to sorbate uptake and contributes to isotherm nonlinearity on solids with low natural organic matter contents *(23).*

Farrell and Reinhard also studied mechanisms responsible for slow desorption using both model solids with controlled properties and natural soil and sediments. Kinetics of adsorption and desorption are among the most influential processes affecting the transport and the fate of contaminants in the environment. In addition, the slow release of sorbed contaminants is the primary obstacle to remediation of soil and goundwater pollution. The results of their study demonstrated that" intraparticle pores of molecular dimensions may be responsible for slow releases of sorbed contaminants" *(24).*

The available literature has been limited in the number of column studies reporting cosolvent effects on sorption and mobility of hydrophobic organic compounds. While the column experiments reported here were not the first to evaluate the competition between sorption and cosolvency, they are unique in their use of cosolvent "pulses" that mimic a typical release event. This study was conducted to compare and contrast the extent of cosolvent effects among three categories of polar organic solvents (an alcohol, an amine, and a ketone) on the sorption and mobility of tetrachloroethylene in the Missoula Valley Aquifer. Cosolvent values for ammonia, the amine used in these column experiments, have not previously been reported in the literature.

CHAPTER 3

EXPERIMENTAL METHODS

Soil Collection

Soil was collected at the construction site of the Gallagher Business Building on the campus of the University of Montana (Figure 3-1). The pit for the building's foundation extended 16 feet below ground level. Soil samples were taken at approximately two, three, five, thirteen, and fifteen feet above the base of the site excavation (Figure 3-2). Samples were air-dried and sequentially sieved to obtain soil fractions that were consistent in particle size to promote reproducible replication. The sieve analysis consisted of a series of 17 sieves with screen openings ranging from 32 mm to 0.0625 mm. Ultimately, soil fractions from 0.35 mm to 0.0635 mm (coarse sand to very fine sand as described in Table 3-1) were combined to produce five "soil" samples.

The soil samples were sterilized in an autoclave at 121° C and 15 PSI. These settings were held for 30 minutes. After an additional five minutes for pressure reduction, the sterilization was complete. Soil samples were subjected to three levels of characterization:

1. Analysis of total carbon *vs.* inorganic carbon (by coulometery) - to obtain the fraction of organic carbon which is important as a sorbent for chlorine-containing hydrocarbons.
2. Acid digestion followed by inductively coupled plasma ICP analysis - to obtain a whole rock analysis of mineral elements.
3. Visible microscopy - to obtain a census of identifiable mineral grains.

Figure 3-1. Site of Soil Collection.

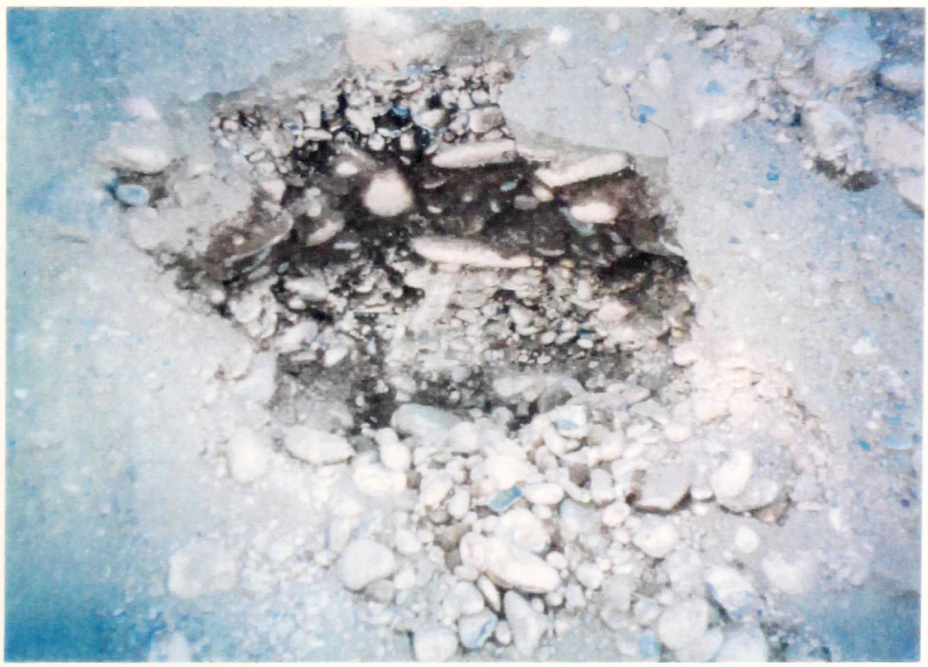


Figure 3-2. Soil-Type "Close-Up".

Table 3-1. Grain-size scale.

Wentworth size classes, equivalent phi (Φ) units, U.S. Standard Sieves numbers corresponding to various millimeter and Φ sizes are listed (From Boggs, 1987, p.107).

	U.S. Standard Sieve Mesh	Millimeters	Phi (Φ) units	Wentworth Size Class
GRAVEL		4096	-12	
		1024	-10	Boulder
		256	-8	----------
		64	-6	Cobble

		16	-4	Pebble
	5	4	-2	----------
	6	3.36	-1.75	
	7	2.83	-1.50	Granule
	8	2.38	-1.25	
	10	2.00	-1.0	
SAND	12	1.68	-0.75	
	14	1.41	-0.50	Very
	16	1.19	-0.25	Coarse Sand
	18	1.00	0.0	----------
	20	0.84	0.25	
	25	0.71	0.50	Coarse Sand
	30	0.59	0.75	
	35	0.50	1.00	----------
	40	0.42	1.25	
	45	0.35	1.50	Medium Sand
	50	0.30	1.75	
	60	0.25	2.0	----------
	70	0.210	2.25	
	80	0.177	2.50	Fine Sand
	100	0.149	2.75	
	120	0.125	3.00	----------
	140	0.105	3.25	
	170	0.088	3.50	Very
	200	0.074	3.75	Fine Sand
	230	0.0625	4.00	
SILT	270	0.053	4.25	
	325	0.044	4.50	Coarse Silt
	-----	0.037	4.75	
	-----	0.031	5.0	----------
	-----	0.0156	6.0	-Medium Silt-
		0.0078	7.0	-Fine Silt-
		0.0039	8.0	-Very Fine Silt-

Column Preparation

The experiments employed a glass column (Pharmacia) that was 40 cm in length and 2.5 cm in diameter. A support base of glass wool was used. The column was packed using the "slurry method" *(12)*. The slurry was prepared by adding the solid sorbent to a quantity of deionized water. The slurry was swirled so that it was thick, flowing, and free from entrapped air bubbles. While pouring, the column was tapped gently to generate an evenly packed column.

The complete experimental apparatus (Figure 3-3) included an eluent reservoir of deionized water to establish a hydraulic head on the column's packed bed. A constant flow rate through the saturated packed column was maintained at approximately 1.5 to 2.0 ml/min during sample collection. The column was never allowed to run dry.

Tetrachloroethylene

All experiments performed in this study employed tetrachloroethylene as the sole hydrophobic organic compound. Some of its chemical characteristics are provided in Table 3-2. Synonyms for tetrachloroethylene include: Ankilostin, Ethylene tetrachloride, PCE, Perchloroethylene, Perclene, PERC, and 1,1,2,2-Tetrachloroethylene. Tetrachloroethylene finds use as a dry cleaning fluid, in degreasing and drying metals and other solids, as a solvent for waxes, greases, fats, oils, and gums; in the manufacture of printing inks and paint removers, and in the preparation of fluorocarbons and trichloracetic acid. Tetrachloroethylene is a colorless liquid with a "chloroform or sweet ethereal odor".

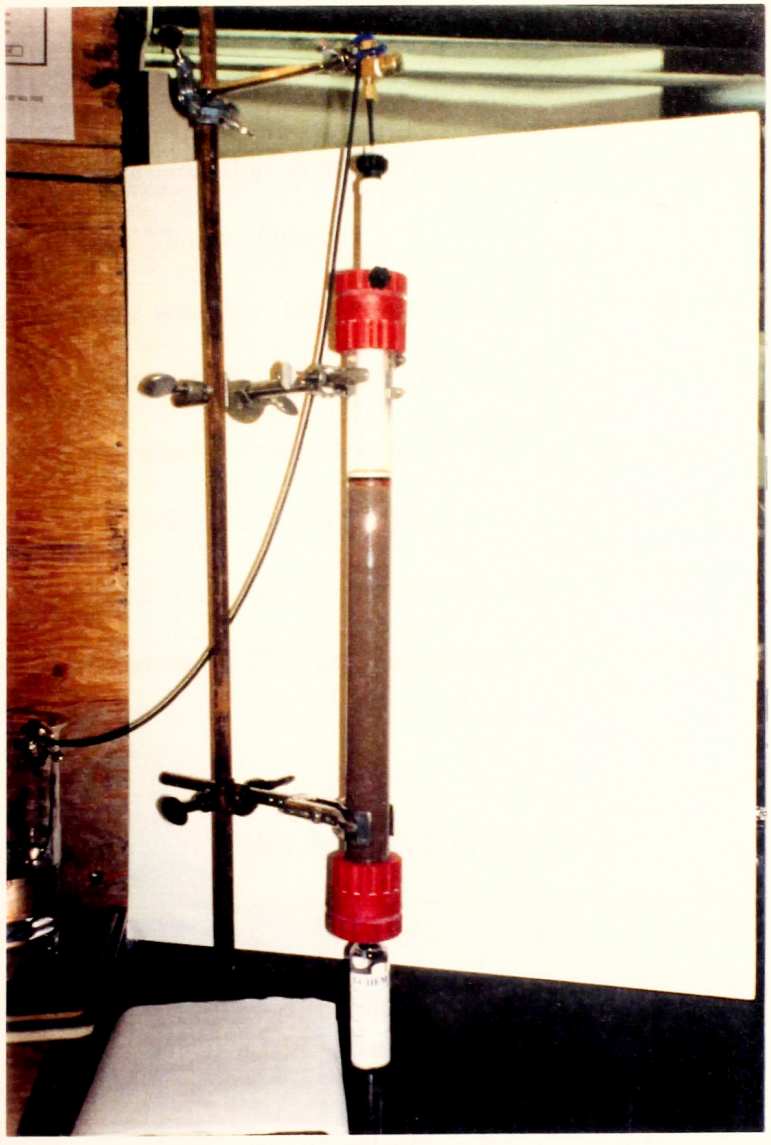


Figure 3-3. Packed Soil Column.

While it is soluble in ethanol, benzene, and ether, tetrachloroethylene is only sparingly soluble in water. Its water solubility has been measured to be 150 mg/L at 25°C ***(13)***.

During an experimental trial, the neat tetrachloroethylene, a typical component found in contaminated ground water, was added to the system into the pre-column eluent flow via a "T" connector. A 10 μl syringe (Hamilton) was used to pierce a brass-bound Teflon septum (Supelco Thermo-Green).

Because of solute volatility, post-column samples were collected in chilled, 40-ml borosilicate glass sample vials (I-CHEM Item G236-0040), made specifically for volatile organic analyses. (Evaporation from water at 25°C of 1 ppm solution is 50% after 24-28 minutes and 90% after 72-90 minutes)***(13)***. Vials were completely filled and immediately capped to eliminate head space and lab atmosphere losses of PCE.

Additional properties of PCE are summarized in the following table:

Table 3-2. PCE Properties

Molec. Weight (g/mol)	Melting Temp. (Tm)	Boiling Temp. (Tb)	Henry's Law Const. (K_H) atm-m^3/mol @25°C	Log K_{oc}	Log K_{ow}	Vapor Pressure at 25°C -log P^o_{atm}
165.8	-19.0°C	121.0°C	0.0153	2.42	2.88	1.60

Four-Step Soil Column Experiment

This study was designed to look at the cosolvent effects on the mobility and subsurface transport of tetrachloroethylene. The column experiments in which acetone and aqueous ammonia were employed as the cosolvent consisted of four steps:

Step 1: Five to ten microliters of tetrachloroethylene (neat compound) were added to the pre-column eluent stream (deionized water). Samples were collected and analyzed until the maximum concentration of PCE had passed and a constant decrease of PCE concentration was observed. (Given the low aqueous solubility of PCE, it was suspected that a significant portion of the chlorinated hydrocarbon would partition to the soil and be retained).

Step 2: A pulse of the cosolvent, (6 ml) was injected onto the column. Again, samples were collected and analyzed until a new maximum concentration of PCE had been observed and a continually decreasing concentration was evident. (It was predicted that the chlorinated compounds would re-partition into the eluent and be present in the solution samples due to cosolvency).

Step 3: Third, additional cosolvent solution was flushed through the column to desorb any remaining compounds.

Step 4: Finally, the column was flushed with water.

Reproducibility of the data was confirmed by re-packing the column with new soil material, giving a total of three data sets for each of the two cosolvents. The purpose of the multiple cycles was to evaluate irreversible binding of PCE to sorption sites. The four-step procedure was not followed with the anti-freeze trials. Instead, the column was re-packed with a fresh slurry three times to confirm reproducibility.

Only one specific soil sample was subjected to this procedure; the other two soil samples had hydraulic conductivities that proved infeasible given the volatile nature of PCE.

The data were plotted as concentration versus fraction number.

Extraction Procedure

Samples were analyzed using EPA Extraction Method 551, "Determination of Chlorination Disinfection By-Products and Chlorinated Solvents in Drinking Water By Liquid-Liquid extraction and Gas Chromatography with Electron-Capture Detection" ***(14)***. (Although the method is specific for Gas Chromatography with an ECD, it was applicable to the Gas Chromatograph/ Mass Spectrometer.) A brief summary of the procedure that was used is as follows:

1. Add 4 mg of dechlorination reagent, ammonium chloride (reagent grade) to the sample vial just before sample collection.

2. Add 70 μl of the internal standard 1,1-dichloro-2-propanone (DCP) to 35 ml of sample via a dispensing pipette (Eppendorf) with disposable tips.
3. Add 8 g of NaCl (reagent grade).
4. Add 2 ml of methyl tertiary-butyl ether (MTBE), (Burdick and Jackson, High Purity) via an Eppendorf dispensing pipette.
5. Invert the sample vial and shake vigorously for 1 minute to dissolve the NaCl and allow the water and MTBE phases to separate.
6. Transfer a portion of the organic phase to a 2 ml clear, autosampler vial with a screw top lid and septum (SUPELCO, cat. no. 2-7078) using a disposable Pasteur pipet.

Notes:

- Samples were refrigerated at 4 degrees Celsius until analysis.
- Samples were analyzed within 14 days of collection.
- A calibration sample was analyzed each day before soil column samples were analyzed. (35 μl of 2000 μg/ml DCP in MTBE and 10 μl of 150 μg/ml tetrachloroethylene in methanol)
- Laboratory blanks of deionized water and the internal standard were analyzed every 20 samples to ensure quality control.

Gas Chromatography Analysis

The instrument utilized for all analyses in this study was a temperature programmable Hewlett Packard G1800A Gas Chromatograph/Mass Spectrometer. It was equipped with a splitless injector, a fused silica capillary column, an electron ionization detector (EID), and an integrated software package to acquire/quantify the data. (Figure 3-4).

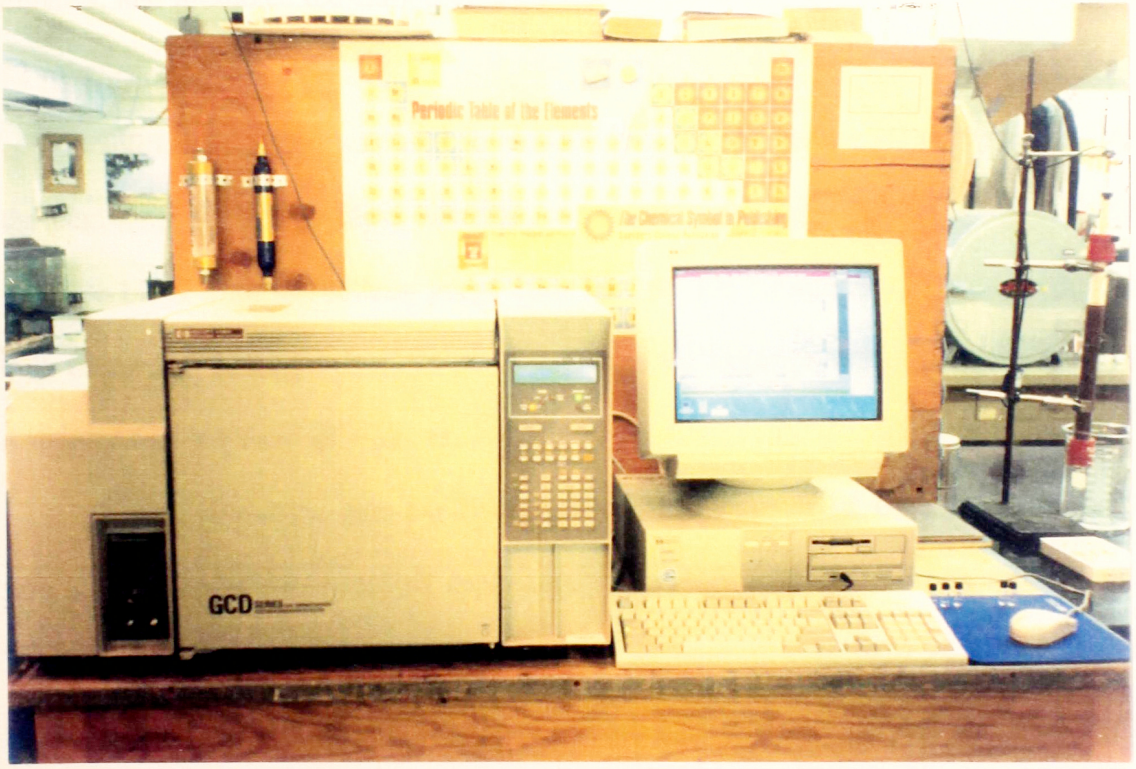


Figure 3-4. Gas Chromatograph/Mass Spectrometer

A complete description of the operating parameters under user control is shown in Table 3-3.

Temperature programming was used to assure an adequate, but rapid, separation of the internal standard (1,1-dichloroactone) from the PCE. While the initial temperature of 40 °C was maintained for 10 minutes, the low boiling MTBE solvent (bp 55 °C) cleared the column and was removed from the inlet area while the detector was off. At 4 minutes, the detector was turned on. The internal standard (bp 117 °C) appeared at approximately the 6 minute mark. The temperature program became activated at 10 minutes, and promoted the elution of PCE (bp 121°C) which appeared at approximately 12 minutes.

Splitless injection was used to enhance analysis for trace level components. At the beginning of each splitless injection, the entire 1 μl sample was volatilized in the injection block with the column purge flow shut off for 1.0 minute. This allowed the bulk of the low boiling solvent to be vented from the injection port. Left behind, was a sharply focused band of analytes.

A methyl silicone gum capillary column (Hewlett Packard Ultra 1 Crosslinked) was chosen for its demonstrated applicability to chlorinated hydrocarbon separations. The column installed was 30m in length, had an internal bore of 0.32 mm and was coated with a 1.0 μm thick film of methyl silicone gum as a stationary phase. Under the conditions experienced in these studies, the column exhibited approximately 120,000 theoretical plates toward PCE.

Table 3-3. Operating Parameters for the GC/MS

Oven Temperature:	**Time:**	**Ramp:**
Initial: 40° Celsius	10.00 minutes	6 °/minute
Level #1: 70° Celsius	1.00 minute	15 °/minute
Level #2: 100° Celsius		

Detector Temperature: 280°C **Injector Temperature:** 220°C

Flow Rates:

Helium: 0.5 ml/min

Pressure at 40° C: 19 Kpa

Solvent Delay: 4.0 minutes

Run Time: 18.00 minutes

Column:

Hewlett Packard Ultra 1 Crosslinked Methyl Silicone Gum Capillary Column

Column ID: .32mm Film Thickness: 1.0 μm

Length: 30m Phase Ratio: 80

The electron ionization detector consisted of four main components -- the electron impact ion source (EI), the quadrupole mass analyzer, the electron multiplier detector and the HP ChemStation software package. The EI ion source receives the sample components as they elute from the capillary column and bombards them with a stream of high energy electrons (about 70 eV). The electrons cause reproducible fragmentation of the molecules. Once the fragmentation has occurred, positive ions in the mixture were accelerated into the quadrupole analyzer. A voltage pattern was applied to the quadrupole such that only one mass/charge (m/z) ratio could successfully travel across the mass analyzer at any point. A signal was generated proportional to the abundance of each ion at the electron multiplier horn (instrument preset gain of 1647 volts). In the experiments reported here, scans ranged from 35 to 260 m/z (although the instruments collects the data from high to low m/z). This process was repeated continuously as a sample eluted. Data were acquired and processed with the HP ChemStation software package which generated retention time, abundance, and mass spectral data ***(15)***.

The chromatographic procedure used for each sample and standard analysis after the instrumental parameters had been established is as follows:

1. Withdraw 1 μl of air and 1 μl of sample into a 10 μl syringe.
2. Introduce contents into the capillary column by injecting through a Thermogreen septum (Supelco #2-3156).
3. Collect data for 18.0 minutes.
4. Allow oven to cool to 40° C before injecting the next sample.

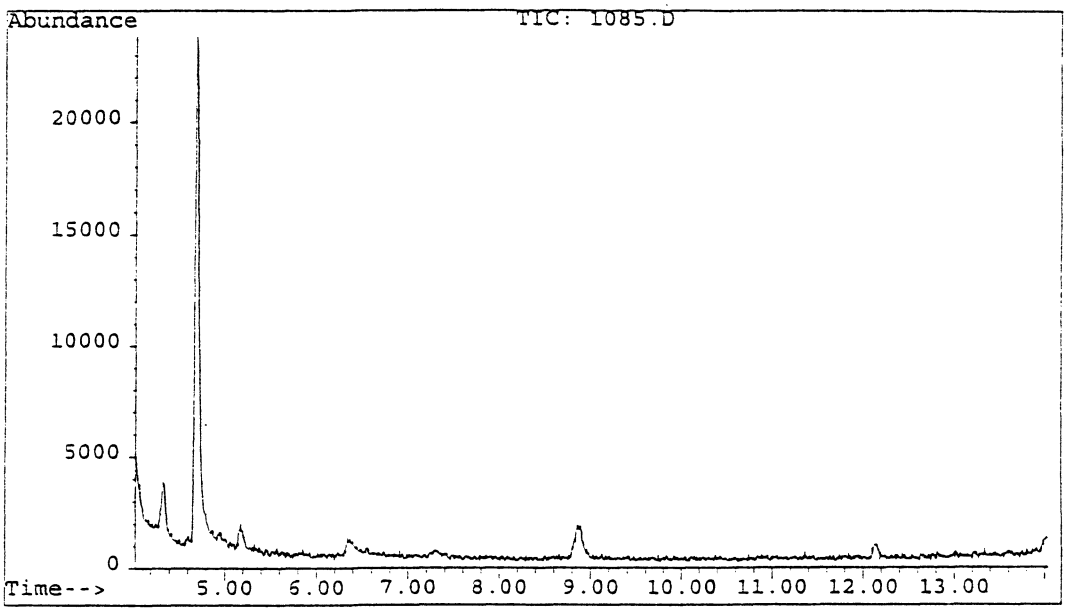
Data Analysis

For the purpose of data analysis, the Hewlett Packard G1800A GC/MS was equipped with a data system that consisted of an HP Vectra 486 personal computer running ChemStation software under Windows for Workgroups. The software that controlled the operation of the GCD collected data from the EID, and provided many options for processing and reviewing those data.

Studies conducted in the chemistry lab during January, 1995, concluded that the Hewlett Packard G1800A GC/MS has a limit of detection between 0.050 μg/ml (Figure 3-5, panel A) and 0.010μg/ml (Figure 3-5, panel B) for the neat compound, tetrachloroethylene. Samples for the study were prepared in three stages of dilution from an original stock solution of 81.15 μg/ml. Note, presence of PCE is confirmed by a peak appearing at approximately 12.00 minutes. This peak is still observable with a concentration of 0.050 μl/ml; however, at a concentration of 0.010 μl/ml a peak is not present.

The software had the capability of peak integration and provided data in terms of analyte peak concentration based on established quantification files. Five calibration standards were prepared from 1 ml of 5000 μg/ml of tetrachloroethylene in methanol (EPA-certified standard) obtained from SUPELCO (Catalog no. 4-0083). Concentration vs. instrument response was plotted and a linear regression was taken (Figure 3-6). The halogenated hydrocarbons (tetrachloroethylene and the internal standard, 1,1-dichloroacetone) were identified by viewing their mass spectra. Since all experiments

A



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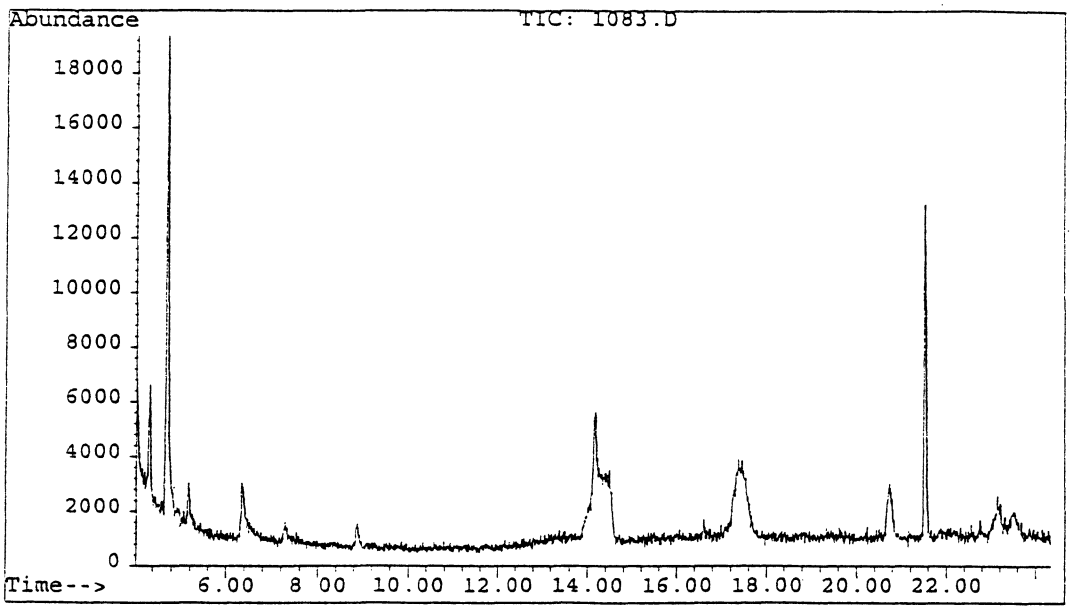


Figure 3-5. PCE Detection Limit. A. Total ion chromatogram for PCE concentration of 0.050 μg/ml. B. Total ion chromatogram for PCE concentration of 0.010 μg/ml.

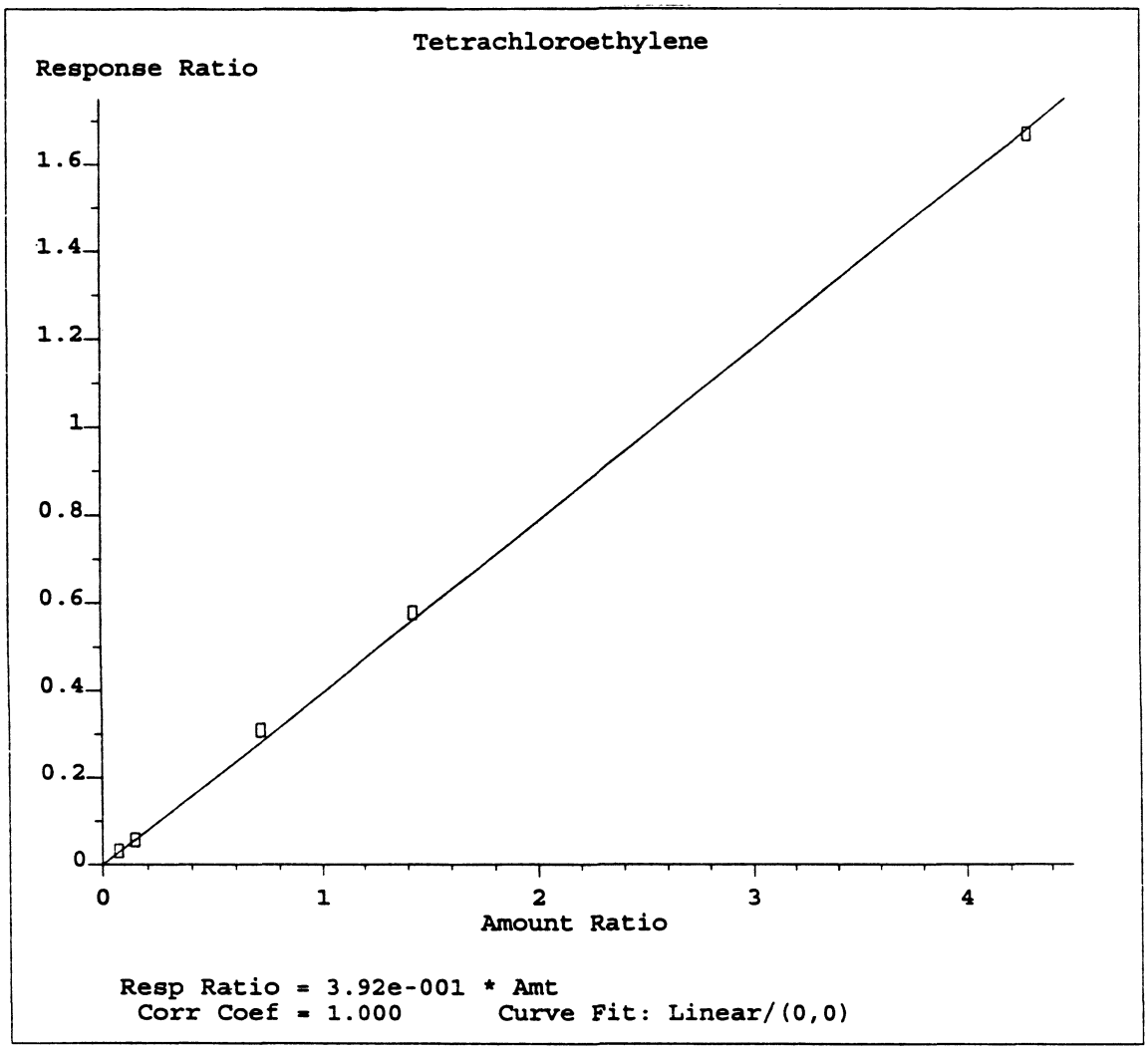


Figure 3-6. PCE Calibration Curve. Concentrations of PCE ranging from 5.00 ng/μl to 300 ng/μl.

were conducted with known synthetic mixtures, peak confirmation with a second column chemistry was omitted. The area of the analyte peak was related to the known peak area of the internal standard via response factors to guard against extraction and injection variability.

CHAPTER 4

SOIL DESCRIPTION AND CHARACTERIZATION

"Soil" refers to the accumulation of particles from disintegrated rock and often decayed organic matter plus a community of microbes and invertebrates. Due to the irregular shape of individual particles, many pore spaces exist between the solid grains. The pore spaces may be filled with a liquid, or gas, making soils a three-phase material or system (solid, liquid, and gas). While particle shape and size have been found to affect the material behavior, other factors are also important. Sorting and mineralogical composition also have significant influence on a soil's properties and behavior ***(16)***.

Soil deposits are considered permeable. In addition, the random arrangement of the soil grains makes it highly probable that the direction of flow and velocity of the fluid will vary considerably. Factors that influence flow are (1) the pressure gradient across which flow is occurring; (2) density and viscosity of the fluid; (3) size, shape, and number of pore openings; and (4) mineralogical or electrochemical properties which affect interfacial surface tensions.

To better understand the behavior and interaction of PCE with the specific soil used in this study, a historical review of the site was explored. In addition, grain-size distributions, coulometric analyses (total carbon *vs.* inorganic carbon), ICP analyses (whole-rock, elemental analysis), and a mineralogical characterization (including the determination of particle shape and size) were completed. The results of this suite of characterizations are summarized in this chapter.

Site History

Soil was collected at the construction site of the Gallagher Business building on the campus of the University of Montana in an effort to obtain an accurate representation of the subsurface material overlying the Missoula Valley Aquifer. The soil consisted of grains ranging in size from cobbles to clay sediment. The geological history of the site suggested that the present soil conditions resulted from climatic changes that occurred over two million years (Oligocene, Miocene, Pliocene, and Pleistocene Epochs) ***(17)***. During this span, the area experienced two, dry, desert-like climates, a tropical environment, and an ice age. A more recent historical overview, illustrated by aerial photographs dating back to the 1920's (Figure 4-1), indicated that the area previously known as the "Clover Bowl" had never been disturbed until the present construction project ***(18)***.

Soil Class

The soil retrieved from the Gallagher excavation fits the descriptive category of "residual soils" ***(16)***. Residual or sedentary soils display a wide range of particle shape, size, and composition with an abundance of fine grains. Residual soil forms from the weathering of rock and the accumulation of organic material. Two principal types of weathering are: (1) Mechanical weathering - induced by wind, rain, running water, ice, and tectonic forces such as earthquakes; and (2) Chemical weathering - disintegration of rock due to chemical reactions in minerals from exposure to atmosphere, temperature

Figure 4-1. University of Montana. 1950 aerial photograph of "Clover Bowl".

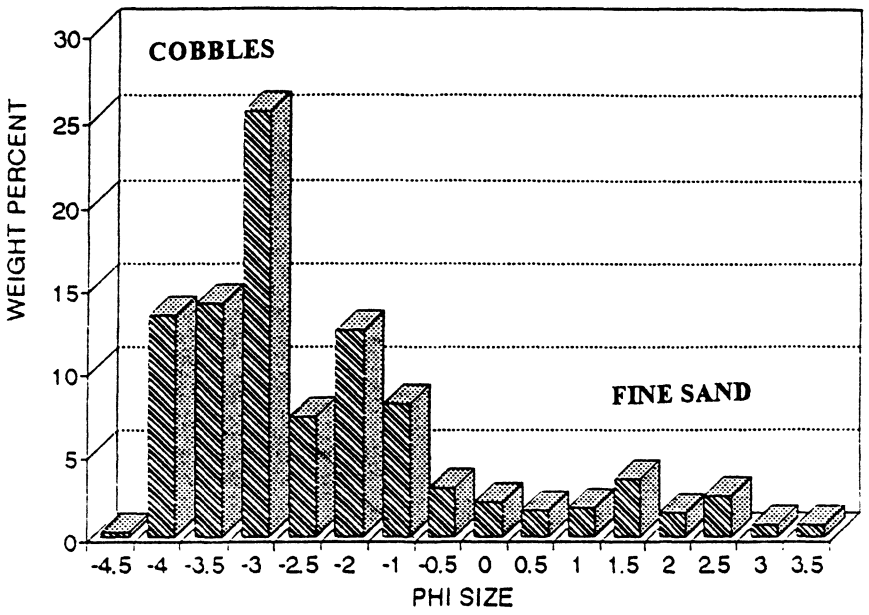
change, water, or other agents. Chemical processes are strongly influenced by climate, topography, drainage, and vegetative cover.

Grain-Size Distributions

Grain-size distributions for the soils were determined with the sieve analysis described in the Experimental Methods (Chapter 3, page 17). Histogram plots and cumulative curves were constructed to visually display the distributions (Figures 4-2 to 4-6). On the histograms, phi size is inversely proportional to grain size (e.g., -4.5Φ corresponds to the largest grain size; +3.5Φ corresponds to the smallest grain size). The cumulative curve is an alternative presentation of the same grain size distribution. It typically has a sigmoid shape in which the slope of the central part of this curve reflects the sorting of the sample. (steep slope = good sorting, gentle slope = pore sorting.)

All five samples were classified as "poorly sorted". Boggs ***(19)*** notes that poorly sorted sediments tend to have lower porosity and permeability than well-sorted sediments. Grains are packed more tightly because pore spaces are occupied by finer sediment. Most natural sediment grain-size populations do not follow a normal curve distribution. The poor sorting character of the samples was borne out in their flow properties when packed into experimental soil columns. Three of the five samples had insufficient hydraulic conductivity for the experimental design even when a peristaltic pump was employed. Too many fine particles inhibited water flow.

A



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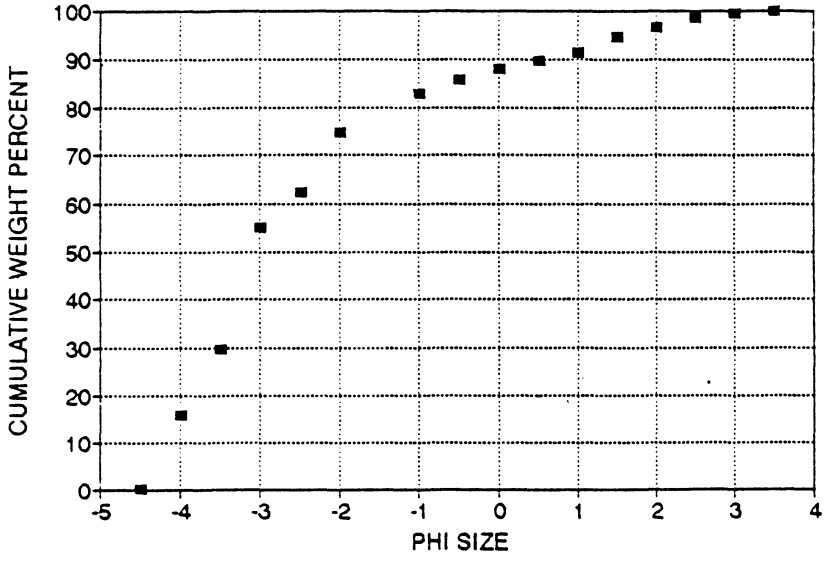
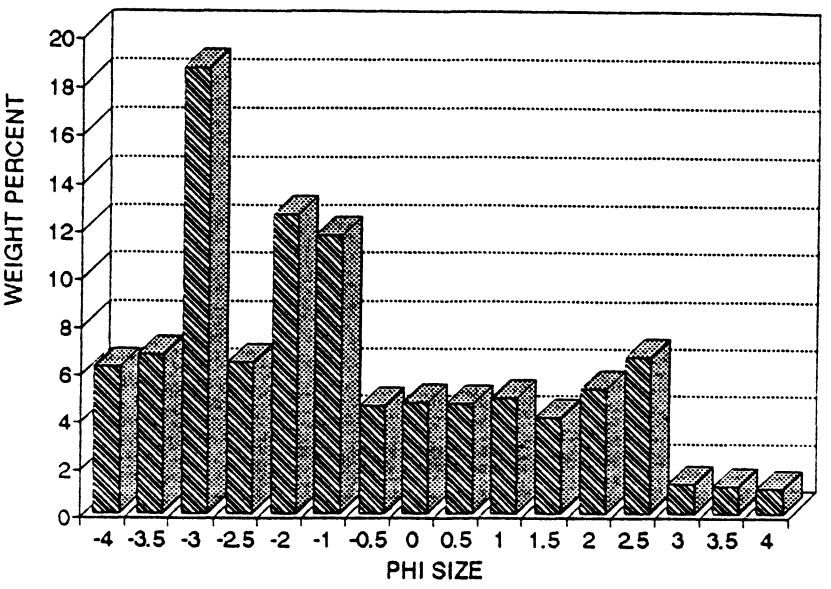


Figure 4-2. Grain-Size Distribution of Soil Sample #1. A. Histogram B. Cumulative curve. Low ϕ values represent cobbles; high ϕ values represent fine-grained sediments. Inspection of the curve shape indicates a poorly sorted soil dominated by fine-grained particles.

A



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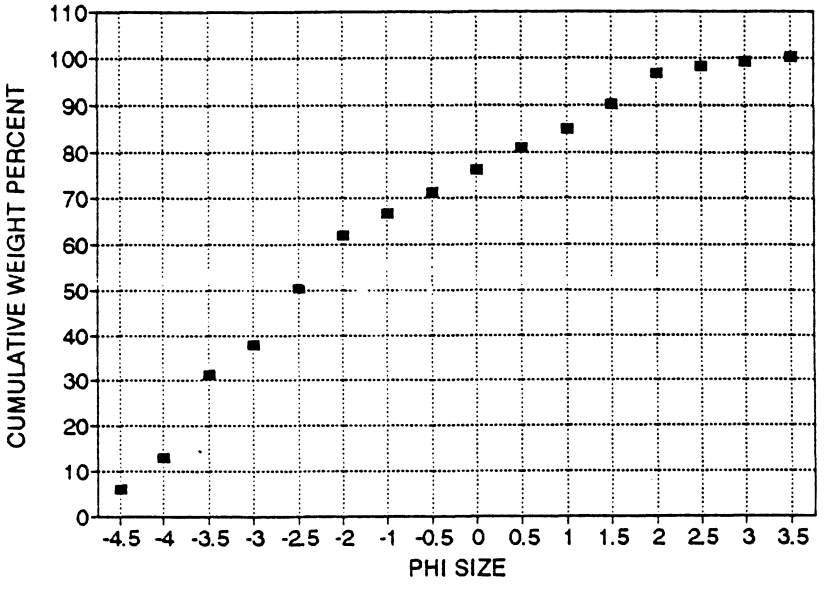
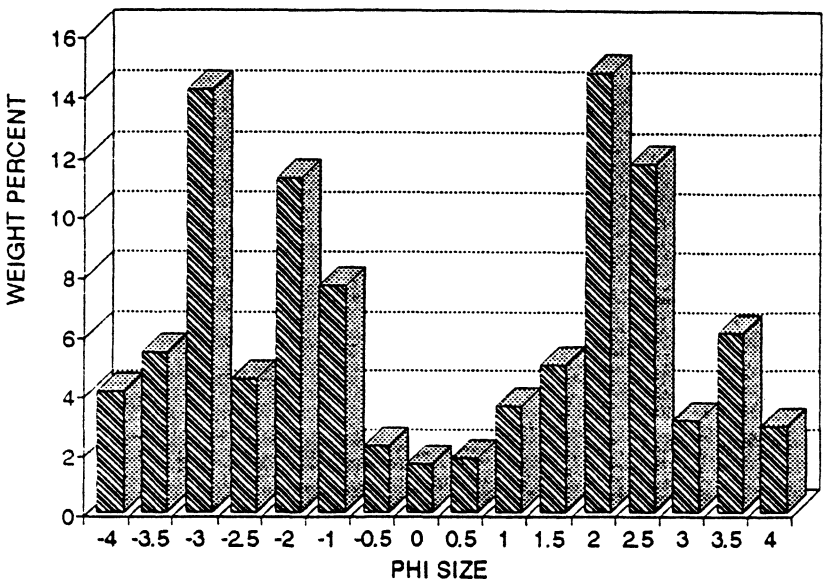


Figure 4-3. Grain-size Distribution of Soil Sample #2. A. Histogram B. Cumulative curve.

A



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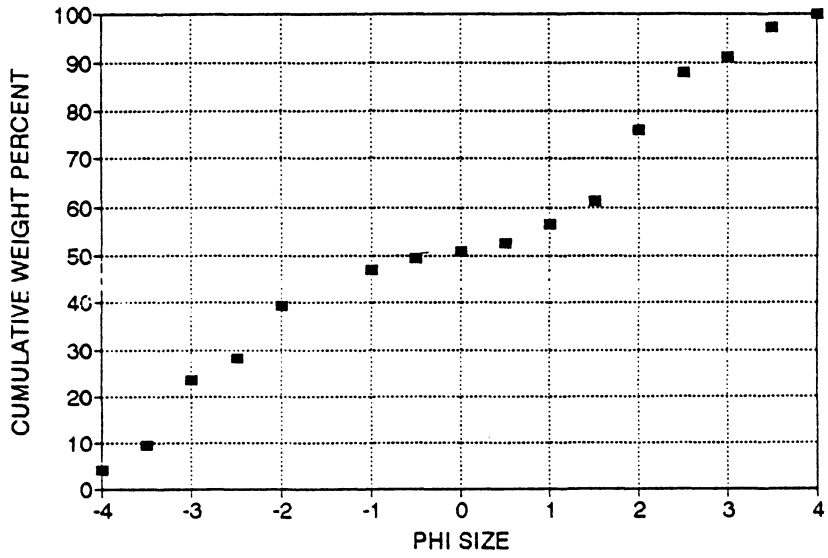
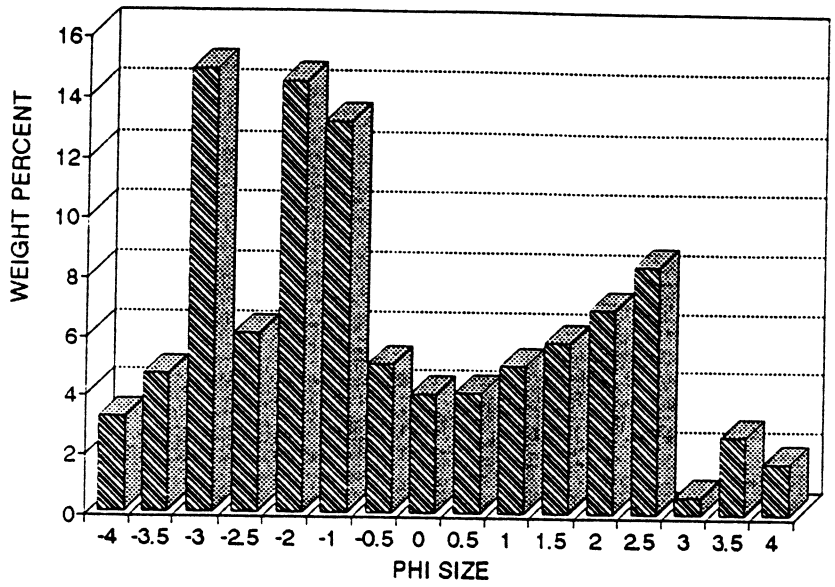


Figure 4-4. Grain-Size Distribution of Soil Sample #3. A. Histogram B. Cumulative curve.

A



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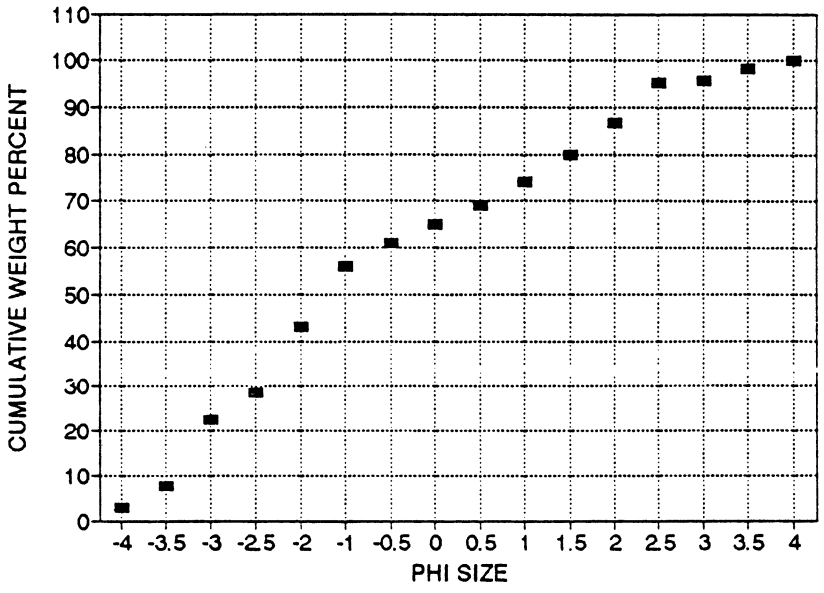
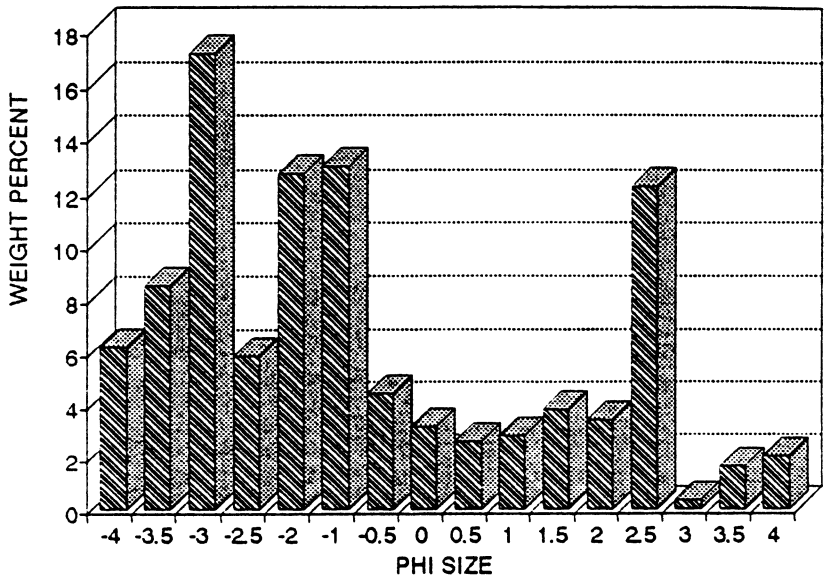


Figure 4-5. Grain-size Distribution of Soil Sample #4. A. Histogram B. Cumulative curve.

A



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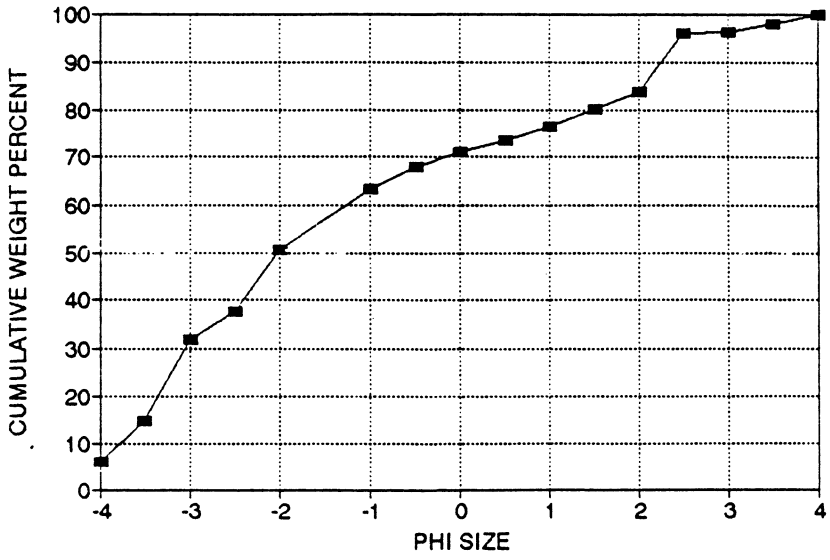


Figure 4-6. Grain-Size Distribution of Soil Sample #5. A. Histogram B. Cumulative curve.

Back-pressures developed when the upper compression cylinder was lowered into position, making contact with the packed bed.

Soil Sample #3 had the best flow characteristics, a flow rate of 2.0 ml/minute from the base of the column was easily achieved when packed with this soil. Its grain-size distribution over the phi range used in column packing (1Φ to 4Φ) is the only one which bears a resemblance to a normal curve. Note that it has higher histogram values in the mid Φ sizes (2Φ to 3Φ) and smaller histogram values to either side. Its cumulative curve between 1Φ and 4Φ has a reasonably good sigmoid profile. Soil samples #1, #2 and #4 all show distinctly non-normal distributions between 1Φ and 4Φ. Soil sample #5 was limited in volume, so it was not tested.

Mathematical calculations were performed on the cumulative curves to extract parametric statistics for normal distributions, i.e., mean, standard deviation and skewness (Table 4-1). The skewness parameter supported that the grain-size distribution for Soil Sample #3 differed significantly from the others. Sample #3's skewness of 0.0512 classified it as "near symmetrical". The skewness of the other samples fell into the "fine skewed" or "strongly fine skewed" categories.

Table 4-1. Calculated Grain-Size Data Parameters.

Soil Sample	Graphic Mean	Standard Deviation	Skewness
1	-2.667	1.669 (poorly sorted)	.4894 (strongly fine skewed)
2	-1.400	2.145 (poorly sorted)	.4260 (strongly fine skewed)
3	-0.483	2.470 (poorly sorted)	.0512 (near symmetrical)
4	-1.000	2.197 (poorly sorted)	.2900 (fine skewed)
5	-1.167	2.260 (poorly sorted)	.6345 (strongly fine skewed)

The following mathematical formulas are for calculating grain-size data of the five soil samples (Boggs, 1987, p. 114).

The graphic mean is the average size of all the particles in a sample and is approximated by averaging phi values taken at the 16th, 50th and 84th percentile.

Table 4-1 (Cont'd). Calculated Grain-Size Data Parameters.

Graphic Mean: $$M_z = \frac{\Phi_{16} + \Phi_{50} + \Phi_{84}}{3} \quad (1)$$

The sorting of a grain population is a measure of the range of grain sizes present and the magnitude of the spread of these sizes around the mean size. Standard deviation is the mathematical expression to represent sorting.

Standard Deviation: $$\sigma_i = \frac{\Phi_{84} - \Phi_{16}}{4} + \frac{\Phi_{95} - \Phi_5}{6.6} \quad (2)$$

Standard Deviation:

$<0.35\Phi$	very well sorted
0.35 to 0.50Φ	well sorted
0.50 to 0.71Φ	moderately well sorted
0.71 to 1.00Φ	moderately sorted
1.00 to 2.00Φ	poorly sorted
2.00 to 4.00Φ	very poorly sorted
$>4.00\Phi$	extremely poorly sorted

Skewness exhibits a certain degree of asymmetry which reflects the sorting in the "tails" of a grain-size population. Positively skewed indicates an excess of fine particles. Negatively skewed indicates an excess of coarse particles.

Graphic Skewness: $$SK_i = \frac{(\Phi_{84} + \Phi_{16} - 2\Phi_{50})}{2(\Phi_{84} - \Phi_{16})} + \frac{(\Phi_{95} + \Phi_5 - 2\Phi_{50})}{2(\Phi_{95} - \Phi_5)} \quad (3)$$

Skewness:

$>+0.30$	strongly fine skewed
+0.30 to +0.10	fine skewed
+0.10 to -0.10	near symmetrical
-0.10 to -0.30	coarse skewed
<-0.30	strongly coarse skewed

Carbon Content

The fate and transport of nonpolar organic compounds in the environment is greatly influenced by sorption to the organic matter fraction of the sediments through which they must move. When high amounts of natural organic matter are present in the soil, hydrophobic organic compounds partition strongly onto it ***(5)***. Soil has two forms of carbon present -- organic and inorganic. The inorganic carbon is present in mineral soil as carbonates, e.g., limestone ($CaCO_3$). Organic carbon is usually in the form of humic substances, often complexed with clay particles ***(20).*** It is important for this study to distinguish between the inorganic and organic carbon contents of the soils.

A coulometric analysis was performed to determine the fraction of organic carbon present in the five soils collected for this experiment. (Note: this analysis was conducted after the soil had been autoclaved.) Actually organic carbon was not directly measured, but derived as the difference between Total Carbon and Inorganic Carbon (Table 4-2 and Table 4-3). Two measurements were made for each sample. In the first, <u>all</u> carbon was converted to carbon dioxide. The soil was weighed in a platinum boat and placed in a ladle that was introduced into a furnace where the sample was combusted in an oxygen atmosphere. There, all carbon was converted to CO_2. In the second, only the inorganic carbon (CO_3^{2-}) was converted to carbon dioxide. Again, soil was weighed in a platinum boat , then heated and acidified with sulfuric acid (H_2SO_4). In both cases, the evolved CO_2 was purged from the reaction vessel and carried to the carbon coulometer by an integrated air pump.

Table 4-2. Coulometric Analysis.

Total Carbon and Inorganic Carbon content in the five different soil samples. Data were obtained coulometrically by Lynn Biegelsen, Department of Geology, University of Montana.

Sample No.	Weight (g)	Micrograms C	% Carbon
Standard 1:	0.0146	1766.2	12.1
Standard 2:	0.0116	1436.5	12.4
Standard 3:	0.0117	1395.7	11.9
TOTAL CARBON			
#1	0.1492	843.7	0.57
#2	0.1885	1321.8	0.70
#3	0.2119	1036.0	0.49
#4	0.0984	1436.5	1.66
#5	0.1338	2136.0	1.60
#4 (duplicate)	0.1144	1903.1	1.66
#4 (triplicate)	0.1175	1957.6	1.67
INORGANIC CARBON			
#1	.5567	2710.6	0.49
#2	.3200	1951.6	0.61
#3	.3066	1146.5	0.37
#4	.1456	782.8	0.54
#5	.1161	853.3	0.74
#4 (duplicate)	.1585	816.7	0.52
#4 (triplicate)	.1450	760.6	0.53
#4 (again)	.1928	1035.6	0.54
BLANK		0.0	

Table 4-3. Calculated Organic Carbon.

Calculated organic carbon content in the five soil samples obtained by subtracting inorganic carbon content from total carbon content.

Sample No.	% Carbon	f_{oc}	* f_{om}
#1	0.08	0.0008	0.0016
#2	0.09	0.0009	0.0018
#3	0.12	0.0012	0.0024
#4	1.12	0.0112	0.0224
#5	0.86	0.0086	0.0172
#4 (duplicate)	1.14	0.0114	0.0228
#4 (triplicate)	1.15	0.0115	0.0230

*Environmental chemistry literature usually uses the fraction of organic matter, f_{om}, instead of % organic carbon (e.g., *5*). A generally accepted conversion utilizes the relationship:

$$2f_{oc} = f_{om} \qquad (4\text{-}1)$$

where:

f_{oc} = fraction of organic carbon = % organic carbon/100; and

f_{om} = weight fraction of solid which is natural organic matter

A coulometer cell was filled with an aqueous solution containing ethanolamine and a colorimetric indicator. The cell was placed between a light source and a photodetector. When a gas stream was passed through the solution, CO_2 reacted with the ethanolamine to form a strong, titratable acid which caused the indicator color to fade. As the percent transmittance increased, the titration current was automatically initiated to generated base electrically. Current ceased to flow when the solution returned to its original color (the original percent transmittance). The coulometer measured the quantity of electric charge (in coulombs) needed to reduce the carbon in the CO_2 produced, and displayed the result as micrograms of carbon. The quantity of electricity required to attain the end point was integrated over the time of its passage. A reaction summary of the coulometric process is as follows:

$$CO_2 + HOCH_2CH_2NH_2 \text{ ------ } HOCH_2CH_2NHCOOH$$

$$Ag^o \text{ ----- } Ag^+ + e^-$$

$$2\ H_2O + 2\ e^- \text{ ----- } H_2\ (g) + 2\ OH^-$$

$$HOCH_2CH_2NHCOOH + OH^- \text{ ----- } HOCH_2CH_2NHCOO^- + H_2O$$

ICP ANALYSIS

A whole rock elemental analysis for the soil samples was obtained from an *aqua regia* digestion. This represents the bulk of the inorganic mineral material except the silicate components. The aqua regia digests were subjected to inductively coupled plasma (ICP) analysis.

The predominant elements present in all five samples were aluminum, calcium, iron and magnesium (Table 4-4 and Figure 4-7). The calcium and magnesium were derived from calcite mineral grains seen in the microscopic identification (following section). The iron and manganese most likely originated from oxyhydroxide films deposited on the quartz grains. The relative concentrations of elements do not vary substantially from one soil sample to another -- calcium > iron > magnesium > aluminum. This suggests all samples contain similar mineral components. Differences in absolute concentrations are probably a result of variations in the quartz fraction of the sample.

MINERALOGICAL CHARACTERIZATION

A microscopic inspection of mineral grains was conducted to finalize soil characterization. This was performed by Chris Greytak, a graduate assistant in The University of Montana Geology Department. Because column experiments were only feasible with Soil Sample #3, it was the only one examined. A summary report of the

Table 4-4. ICP Analysis.

A whole rock analysis of the five different soil samples. Data were obtained by Lynn Biegelsen, Department of Geology, University of Montana. Values are expressed in ppm/gram of soil.

	Det. Limit (ppm)	Soil Sample #1	Soil Sample #2	Soil Sample #3	Soil Sample #4	Soil Sample #5
Al	0.070	3301.89	4896.54	1416.41	6839.21	4549.55
As	0.070	0.00	0.00	0.00	0.00	0.00
Ca	0.100	13950.25	18003.44	12601.15	18251.25	25359.69
Cd	0.010	0.0000	0.0000	0.0000	0.0000	0.00
Co	0.030	4.48	5.00	3.02	5.99	5.57
Cu	0.010	48.90	91.50	30.88	90.16	86.07
Fe	0.030	8059.03	10881.20	4395.75	11331.82	8928.13
Mg	0.100	4797.28	8071.87	3614.28	5555.60	5613.32
Mn	0.005	256.62	277.07	181.79	467.61	328.06
Mo	0.010	11.80	15.70	6.56	16.30	12.89
Na	0.100	46.37	59.65	26.86	106.30	97.83
Ni	0.200	5.72	6.73	2.93	7.42	7.50
P	0.100	250.90	247.30	214.90	411.15	465.40
Pb	0.100	13.75	21.17	0.00	20.96	15.58
Si	0.100	284.02	183.00	152.39	212.60	182.36
Sr	0.005	10.90	14.14	9.37	19.52	17.45
Ti	0.005	87.41	108.91	35.51	259.83	123.57
Zn	0.005	39.91	61.58	19.64	62.04	74.74

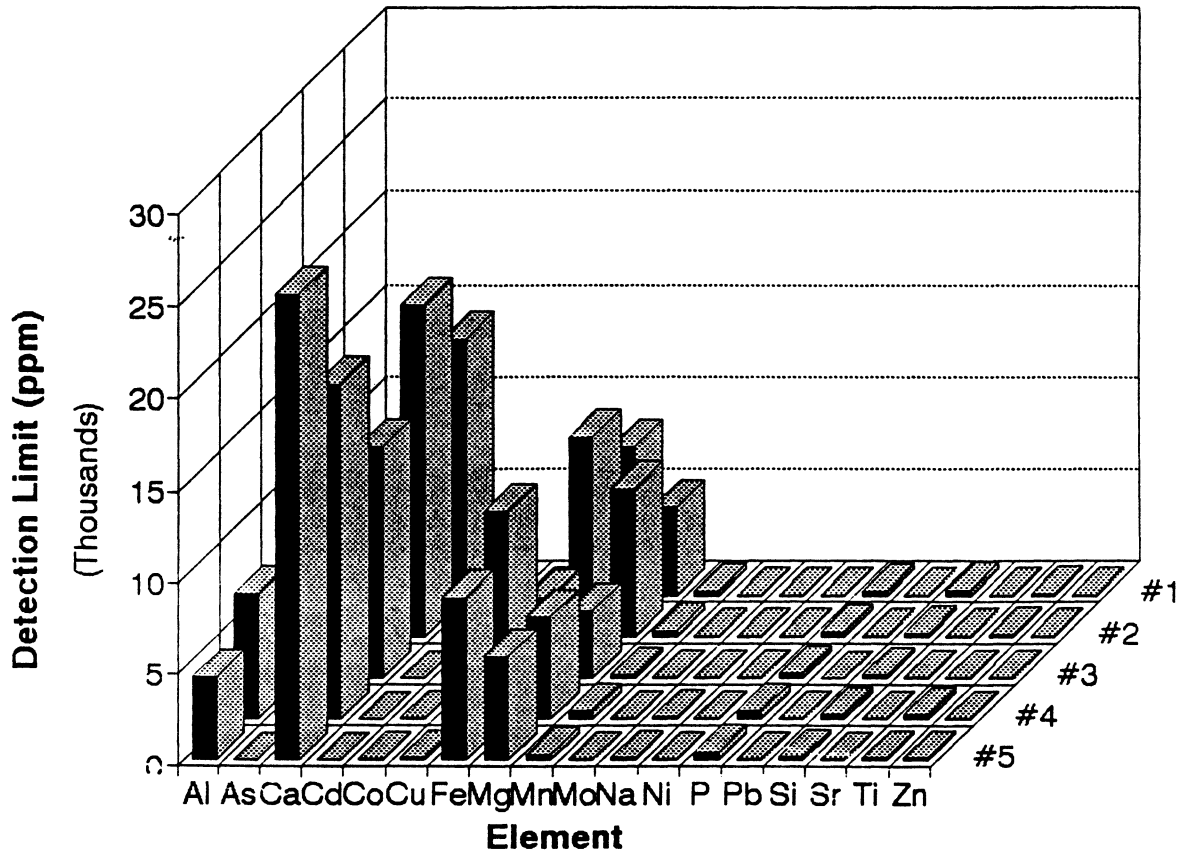


Figure 4-7. ICP Analysis. Elemental Concentrations are in ppm.

identifiable mineral phases is presented as Table 4-5. Note that the large proportion of quartz in the sample suggests that it is the dominant mineral phase. Thus, the rationalization for the absolute concentration trends noted in the ICP data are plausible.

Table 4-5. Mineralogical Characterization

% Composition	Mineral	Description	Shape
73.3	Quartz	Clear, rose, and smokey colored grains.	Angular
		Milky colored grains.	Sub-angular
		Rock fragments made up of several grains of quartz.	
6.7	Feldspars	Types of feldspars were not differentiated.	Subrounded
1.4	Calcite		Angular
18.6	Other	Garnet grains as well as some olivine, micas, hornblende and other unidentified grains.	

CHAPTER 5

COSOLVENCY

The Tetrachloroethylene-Water System

When referring to solubility in water, hydrophobic organic compounds are considered to be insoluble; however, all organic compounds are soluble in water to some extent. Their dissolution can be explained by considering the establishment of a dynamic phase equilibrium. When an immiscible organic liquid comes in contact with water, some of the organic molecules leave the organic phase and dissolve into the water. Conversely, some water molecules enter the organic liquid. Eventually, so many organic molecules enter the aqueous phase that some will begin to return to the organic phase. When the rates of transfer are balanced, the system reaches a dynamic equilibrium and the abundance of the organic molecules in the water is the water solubility of that liquid organic compound *(5)*. Those compounds that have a concentration in water at saturation that is much less than 1 mole/liter ($C^{sat}_{w} << 1$ M) are considered to be "moderately" or "sparingly" water soluble. Tetrachloroethylene falls into this category with $C^{sat}_{w} = 9.12 \times 10^{-4}$ M *(5)*.

Water molecules and organic molecules differ from each other in two ways: (1) they have very different shapes and sizes, and (2) organic molecules are usually much less polar than water. The differences between solute and solvent result in various enthalpic contributions to the excess free energy of solution *(5)*.

Figure 5-1 exemplifies the transfer of an organic solute from its pure liquid phase into water on the molecular level. Changes in interactions between solute:solute, solute:solvent, and solvent:solvent molecules when a liquid organic compound is dissolved in water comprise the enthalpic contributions to the excess free energy of solution.

Column Studies

Initially, the experiment began by injecting six microliters of neat tetrachloroethylene into the eluent flow of water and monitoring the emergence of tetrachloroethylene from the soil column. After a 48-hour period of irregularly collecting samples, an exponential decrease in concentration of tetrachloroethylene was found in the samples (Figure 5-2). This indicated that much of the compound (approximately 91.2 %) had sorbed to the soil and reached a steady state desorption into the eluent stream which explained why trace levels were present even after two days. The first three fractions were collected within the first 24 hours. Fraction four was the first fraction collected on the second day. As a safety precaution, the flow rate was significantly slowed down at night by lowering the water reservoir. The next day, the flow rate of 1.5 ml/min. was resumed. Decreasing the flow and then raising it again, might have been the cause for the unusual increase in PCE concentration in fraction four. In essence, the data formed a classical Lorentzian chromatographic peak with rather severe tailing. This is indicative of some PCE molecules having difficulty in returning into the mobile column eluent phase from stronger sorption sites.

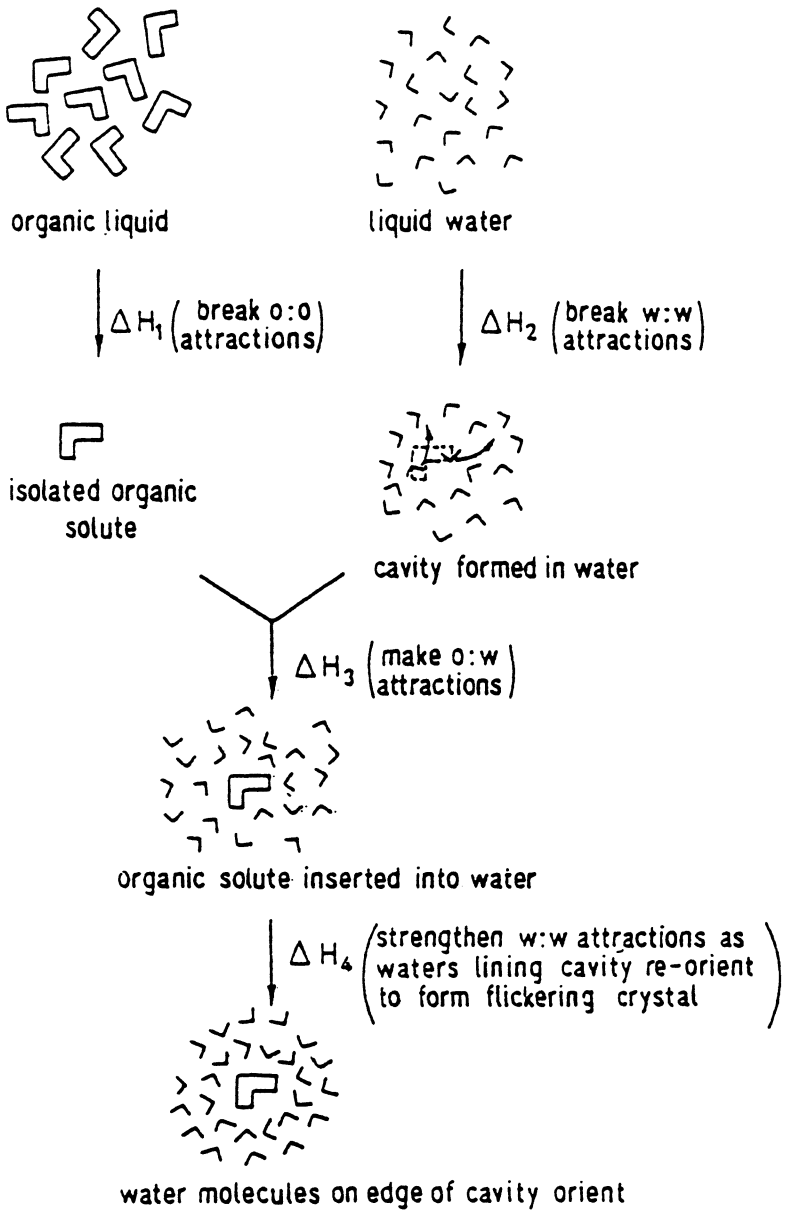


Figure 5-1. Cosolvent Enthalpy Contributions. Schematic representation of the various enthalpies involved when dissolving a neutral organic molecule in water (From Schwarzenbach, 1993, p. 83).

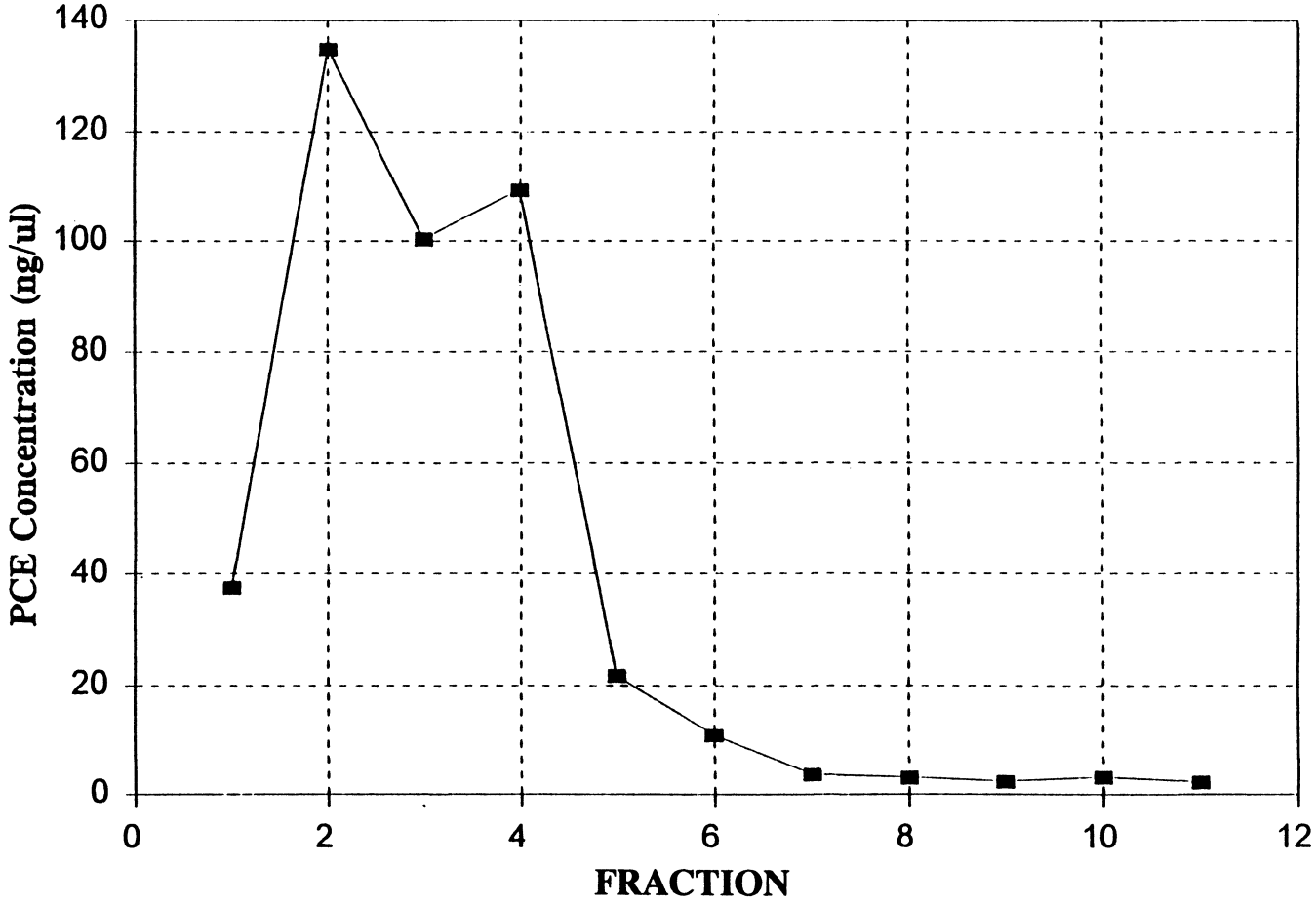


Figure 5-2. Exponential Decrease of PCE Concentration. Fractions were collected over a 48 hour period. (First 24 hours: fractions 1-3. Second 24 hours: fractions 4-11).

Based on the preliminary experiment of monitoring PCE's behavior within the soil column, a procedure that would remain consistent throughout the study was designed. Factors considered were the time frame of one column experiment and the number of samples collected. Ultimately, only one column experiment could be conducted on a given day and led to a total of 16 sequential fractions being collected.

Before injecting PCE onto the column, the first fraction was collected as a "blank", and any residual PCE was determined by analyzing the MTBE-extract via the gas chromatograph/mass spectrometer. Upon placing the vial below the column for fraction two, six microliters of PCE (neat compound) were injected into the column inlet.

Following the injection, a total of seven fractions were collected. The objective was to observe the peak PCE concentration and its subsequent decline before introducing a cosolvent into the system. As fraction nine was collected, six milliliters of cosolvent were injected into the pre-column eluent stream. An additional seven fractions were collected in order to clearly discern the magnitude of PCE mobilized by the cosolvent "pulse".

Anti-freeze as a Cosolvent

The first cosolvent column study mimicked a probable situation at an automotive repair facility (Table 5.1 and Figure 5-3). Since PCE is a common component of carburetor cleaners and degreasing agents, it is not unlikely that some of it will be unintentionally spilled on the ground or find its way into a floor drain. Even more likely is that some of the common 50/50 mix of anti-freeze and water (deionized) used for

Table 5-1. PCE Mobility with Anti-Freeze as Cosolvent - Trial #1.

Fraction	Concentration (ng/μl)
1	0.4
2	1.2
3	1.2
4	25.5
5	38.2
6	26.8
7	25.2
8	26.9
9	23.1
10	40.9
11	282.0
12	182.4
13	186.5
14	158.9
15	154.1
16	46.8

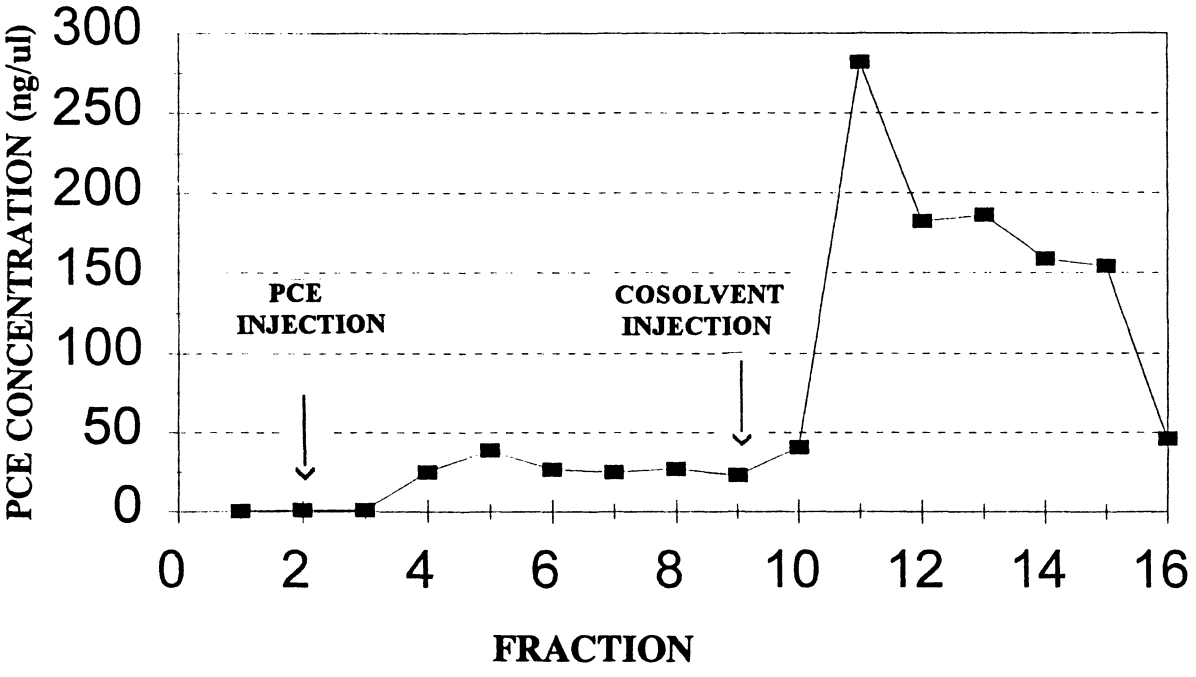


Figure 5-3. Cosolvency Enhancement Curve with Anti-Freeze - Trial #1.

radiator protection will end up in the same vicinity, magnifying PCE levels (cosolvency) and facilitating its movement into ground water.

As fractions were collected, an obvious color change from clear to fluorescent green (fluorescein colorant) indicated that the anti-freeze had cleared the column. The maximum concentration of PCE seen after cosolvent injection (fraction 11, 282 ng/μl) exceeded the pre-cosolvent maximum (fraction 5, 38.8 ng/μl) by a factor of 7.26. The cosolvent maximum exceeds the minimum PCE concentration immediately preceding it (fraction 9, 23.1) even more -- an enhancement of 12.2. Hence, cosolvency represents a substantial increase in PCE mobility under the dynamic constraints of column flow.

Figure 5-4 displays an example of the actual chromatographic data collected for a point in the cosolvency enhancement curve. Figure 5-4 is a typical total ion chromatogram (TIC) for a fraction and shows three peaks -- one for the ethylene glycol in anti-freeze (5.65 min), one for the internal standard (6.44 min) and one for PCE (12.33 min). The mass spectral data (Figure 5-5) shows the molecular ion for ethylene glycol at 62 m/z in the top spectrum, the molecular ion for 1,1-dichloroacetone at 126 m/z in the middle spectrum and the characteristic halogen isotopic fingerprint for PCE around the base peak at 166 m/z in the bottom panel.

In order to demonstrate reproducibility in the experiment, the column was emptied, re-packed with a new slurry fraction of soil sample #3, and the above procedure (p. 57) was repeated. The results are exemplified in a second cosolvency enhancement curve (Table 5-2 and Figure 5-6). This time, the pre-cosolvent concentration of PCE reached a maximum of 77.4 ng/μl and the post-cosolvent maximum was 714.4 ng/μl, demonstrating an enhancement of 9.23. Note that fraction six, not fraction five, had the

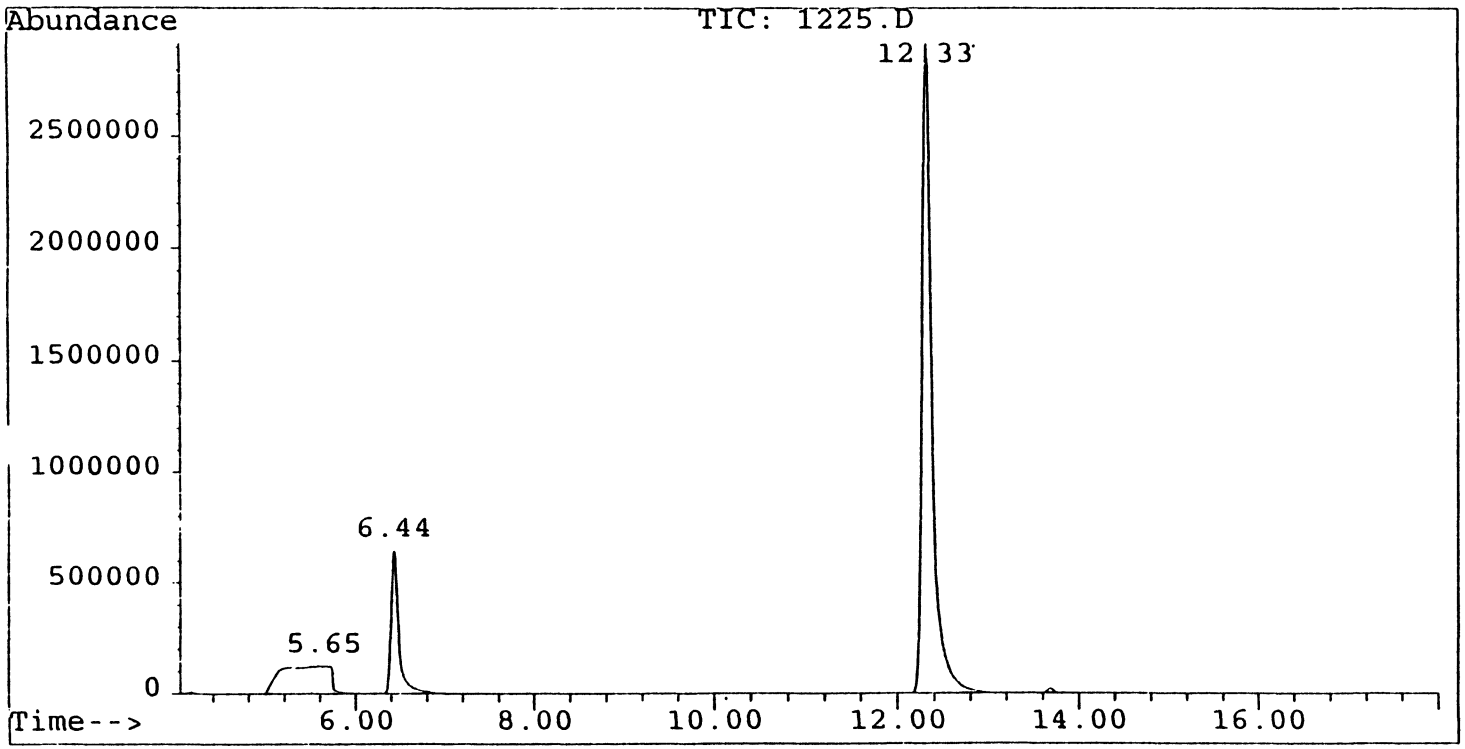


Figure 5-4. Total Ion Chromatogram. The peaks in the chromatogram illustrate the presence of ethylene glycol, internal standard, and PCE.

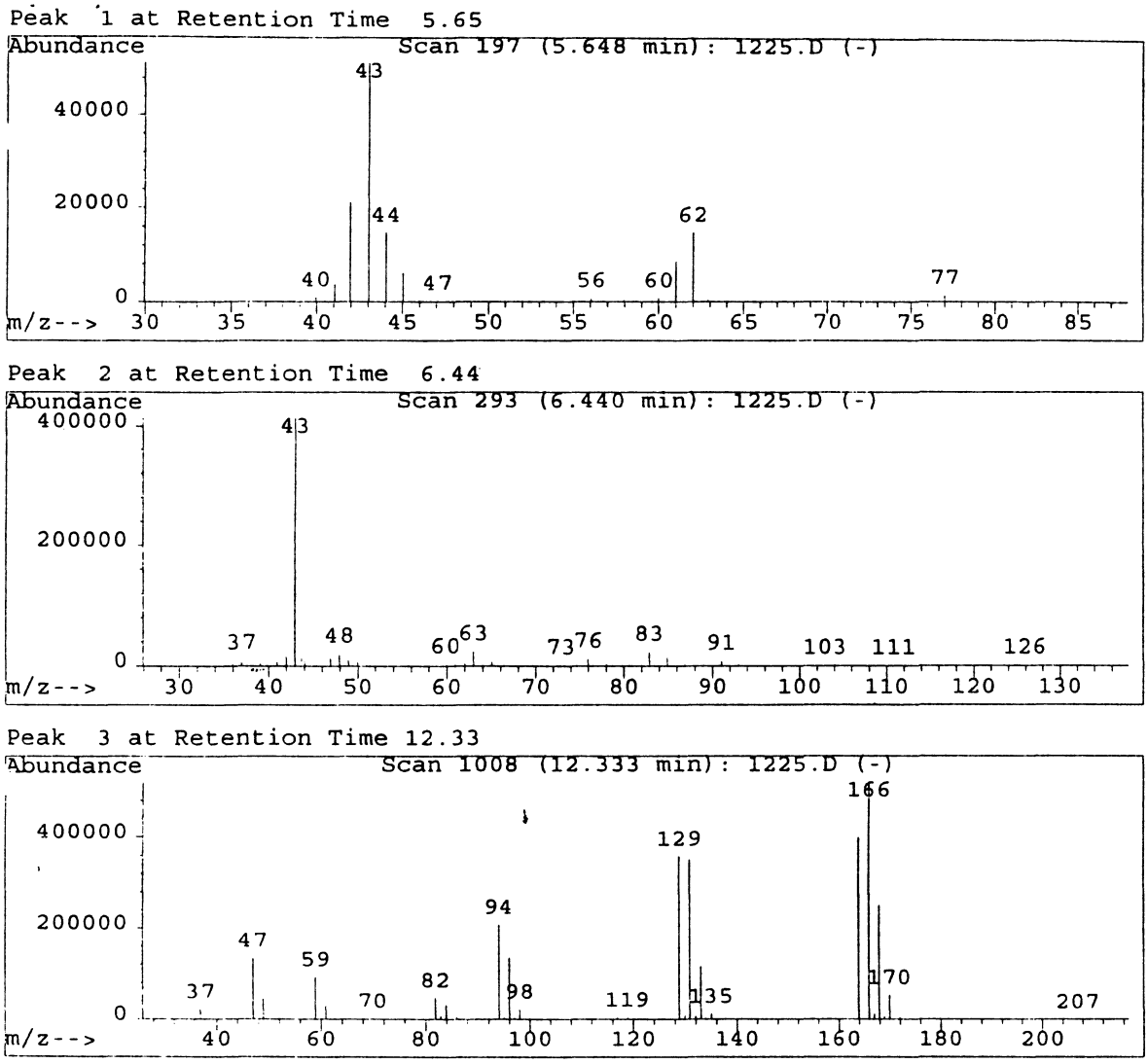


Figure 5-5. Mass Spectral Data. Spectra for ethylene glycol, 1,1-dichloroacetone (Int. std.), and PCE.

Table 5-2. PCE Mobility with Anti-freeze as Cosolvent - Trial #2

Fraction	Concentration (ng/μl)
1	9.8
2	3.5
3	28.1
4	76.0
5	69.7
6	77.4
7	56.3
8	52.4
9	48.8
10	166.0
11	714.4
12	339.9
13	448.7
14	226.9
15	308.1
16	205.2

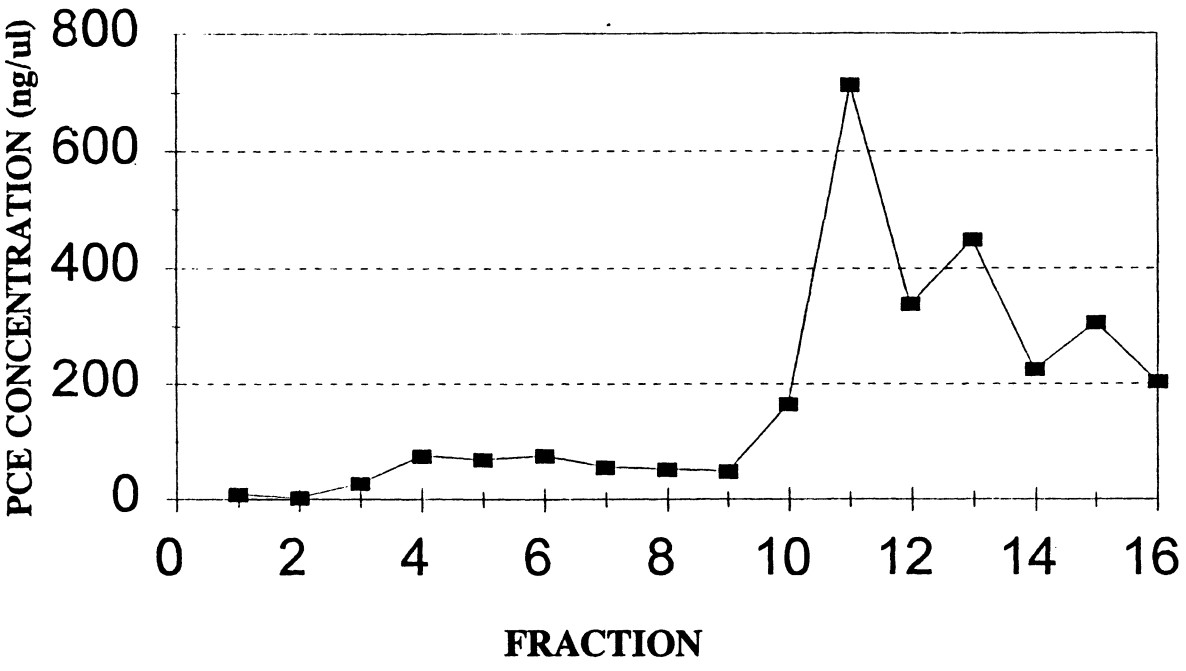


Figure 5-6. Cosolvency Enhancement Curve with Anti-Freeze - Trial #2.

greatest PCE concentration. A slight decrease in PCE concentration was observed in sample five. This unusual pattern could be a result, among others, of a temperature change, column movement, an unnoticed change in eluent flow rate or an inhomogeneous dispersal of the original PCE injection.

The PCE concentration had decreased to a minimum of 48.8 ng/μl before the cosolvent was injected. The enhancement observed between this minimum and the cosolvent maximum was 14.6. Again, substantial cosolvent effects were observed and they were comparable to the first column experiment.

A third column experiment using anti-freeze as the cosolvent was performed. Again, the column was re-packed and the procedure repeated. This time, the profile of the PCE elution curve varied from the first two trials. Table 5-3 and Figure 5-7 depict the disparate results. Sample five contained a maximum PCE concentration of 384.9 ng/μl! This was before any cosolvent had even been added and was five times the pre-cosolvent maximum on Trial #2 and nearly 13 times the pre-cosolvent maximum on Trial #1. Apparently, the PCE was able to find a "quick" way out of the column, i.e., a channel, which limited sorption activity.

With fraction six, the PCE concentration decreased to 190.3 ng/μl. Nonetheless, the decrease did not continue as would be expected if some PCE was being retarded by a sorption-desorption event. Instead, fractions seven and eight again exhibited elevated PCE concentrations of 249.5 ng/μl and 257.1 ng/μl, respectively. A second decline followed in the concentration observed with fraction nine (202.6 ng/μl). Perhaps a second portion of the original injection was swept into the channel system.

Upon injection of the anti-freeze at the beginning of fraction nine, the PCE

Table 5-3. PCE Mobility with Anti-freeze as Cosolvent - Trial #3.

Fraction	Concentration (ng/μl)
1	13.7
2	53.8
3	119.8
4	330.9
5	384.9
6	190.3
7	249.5
8	257.1
9	202.6
10	330.4
11	373.4
12	104.2
13	69.4
14	85.7
15	63.2

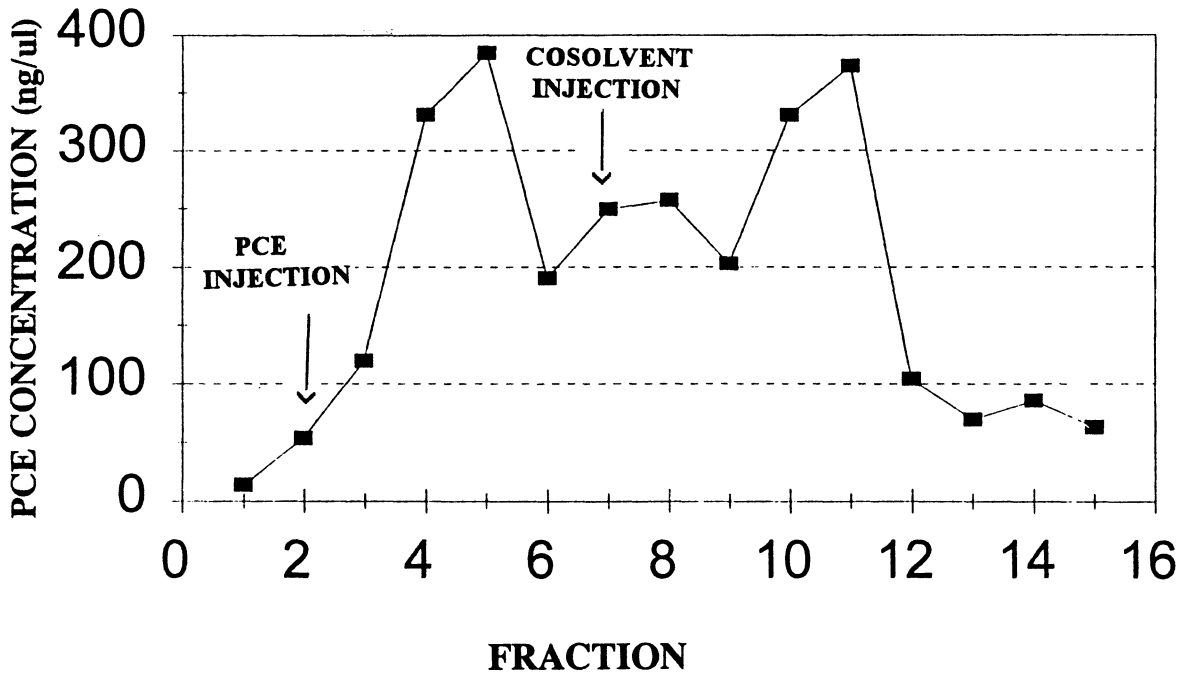


Figure 5-7. Cosolvency Enhancement Curve with Anti-Freeze - Trial #3.

concentration still showed an increase, however, it was not as dramatic as the increases seen with the first two anti-freeze trials. The maximum in this case again appeared at fraction 11 and was 373.4 ng/μl. Comparing this value to the pre-cosolvent maximum of 384.9 ng/μl suggests that the relative amount of PCE remaining to be mobilized in the column was not sufficient to see a higher PCE peak from the anti-freeze pulse. The jump in PCE between fraction 9 at 202.6 ng/μl to fraction 11 at 373.4 ng/μl demonstrates a cosolvency enhancement of 1.84.

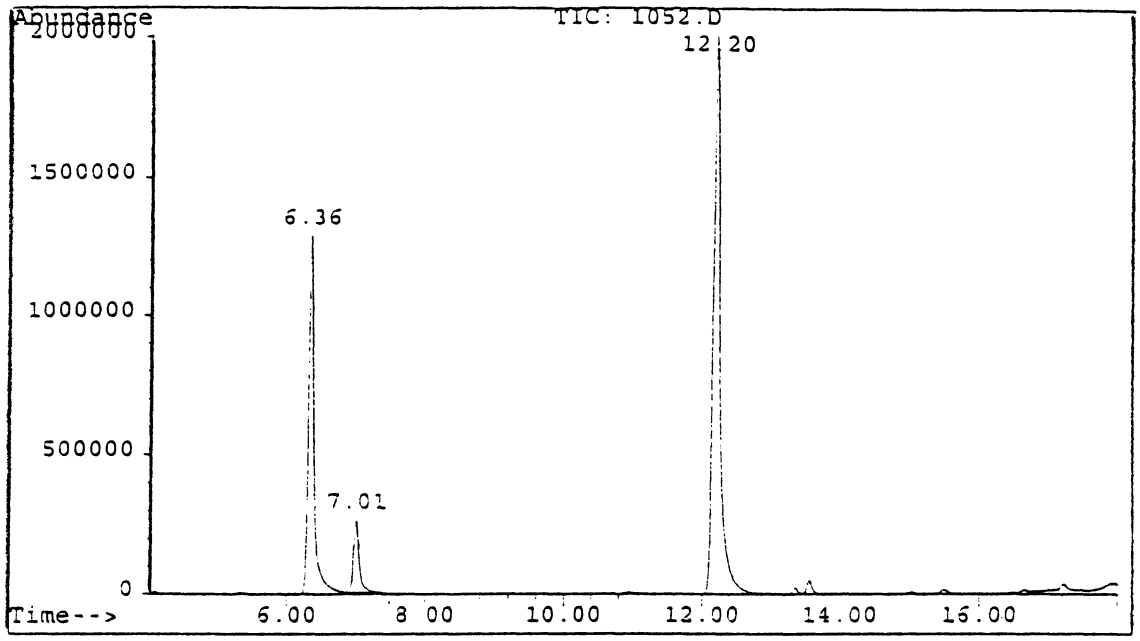
Acetone as a Cosolvent

The second cosolvent used in this study was reagent grade acetone. It is a component of diverse household items (fingernail polish remover and furniture strippers) and, as seen in Table 1-1 (page 10,) is a better cosolvent than ethylene glycol for pyrene.

As samples were collected, a strong ketone smell provided evidence for when acetone was present in collected fractions. A chromatographic peak appearing at approximately 7.0 minutes on the TIC was identified by the mass spectometer as acetone (Figure 5-8). The mass spectral base peak at 43 m/z was assigned to CH_3CO.

Cosolvency trials with acetone were conducted with a freshly packed column. Results from the sixteen fractions that were collected are displayed in Table 5-4 and Figure 5-9. As with Trial #2 of the anti-freeze data, the maximum pre-cosolvent concentration after a slight dip at fraction 5.

A



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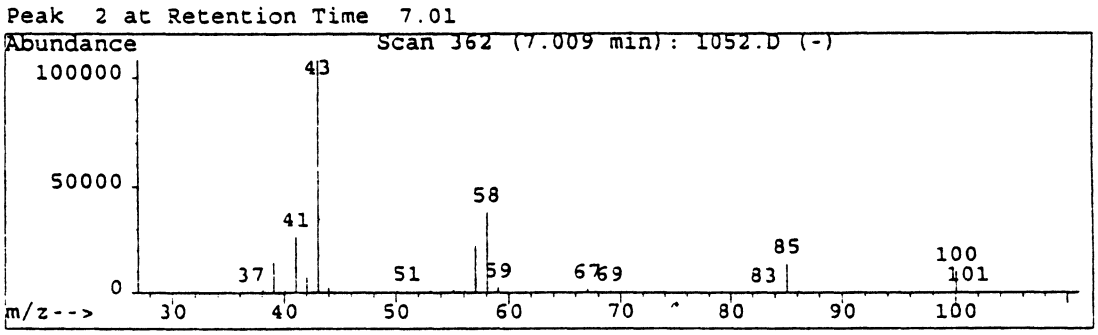

Figure 5-8. Acetone Cosolvency Trial 1. A. Total Ion Chromatogram. B. Mass Spectrum of Acetone peak at 7.0 minutes.

Table 5-4. PCE Mobility with Acetone as Cosolvent - Trial #1

Fraction	Concentration (ng/μl)
1	8.1
2	15.6
3	114.7
4	217.4
5	180.5
6	247.7
7	176.9
8	186.4
9	310.3
10	1356.0
11	130.8
12	41.9
13	40.0
14	24.2
15	15.2
16	12.8

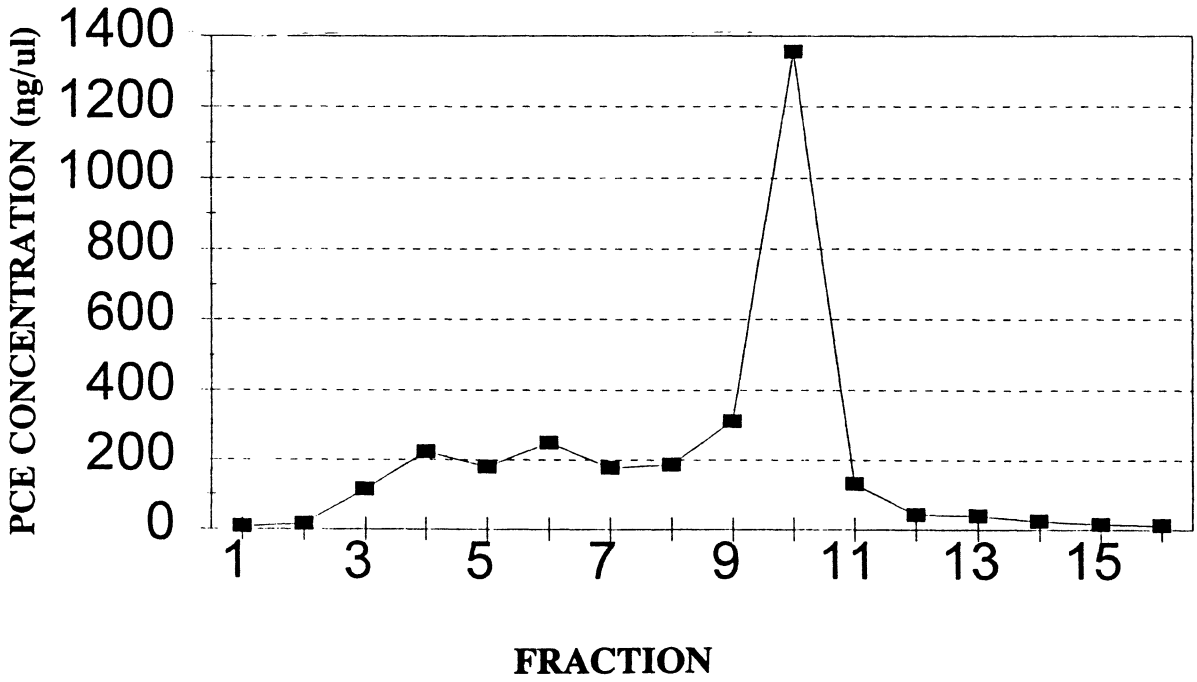

Figure 5-9. Cosolvency Enhancement Curve with Acetone - Trial #1.

The highest pre-cosolvent level observed was in fraction six (247.7 ng/μl). After the addition of acetone, the maximum PCE concentration was 1356.0 ng/μl in fraction 10. This represented a cosolvent enhancement of 5.5 over the peak in fraction 6. The enhancement between fraction 7 (the minimum before acetone was injected) and fraction 10 was 7.7. It seemed unusual that the maximum concentration occurred with fraction 10 instead of fraction 11, as with the three anti-freeze trials. Perhaps the acetone was able to clear the column much faster because it imparted a lower surface tension to the eluent phase or had a lower viscosity than the anti-freeze mix.

At the completion of Trial #1, the column was flushed with 12 ml of acetone followed by water overnight (12 hours). The standard procedure was repeated the next day for acetone Trial #2, and another sixteen fractions were collected (Table 5-5 and Figure 5-10). The maximum pre-cosolvent PCE concentration was 94.5 ng/μl in fraction five. Both samples 11 and 12 had a maximum post cosolvent concentration of 431.3 and 431.6 ng/μl. The enhancement between the pre-cosolvent maximum and the post-cosolvent maximum was 4.6. The PCE concentration in fraction nine was magnified 16.8 times in fraction 11. Since the column was not repacked between Trial #1 and Trial #2, fraction 10 was expected to contain the maximum concentration of PCE as in the first trial. This was not the case, however. Perhaps the acetone from Trial #1 run altered the column packing, coating some soil particles as has been suggested by Rao ***(6).*** Coated particles would provide a greater number of sorption sites for PCE, which is consistent with the overall low concentrations of PCE observed for the run (1356 ng/μl for Trial #1 vs. 431.6 ng/μl for Trial #2).

Table 5-5. PCE Mobility with Acetone as Cosolvent - Trial #2

Fraction	Concentration (ng/μl)
1	1.6
2	1.4
3	49.7
4	87.8
5	94.5
6	45.8
7	25.7
8	27.2
9	27.2
10	133.0
11	431.3
12	431.6
13	160.3
14	60.3
15	51.0
16	24.5

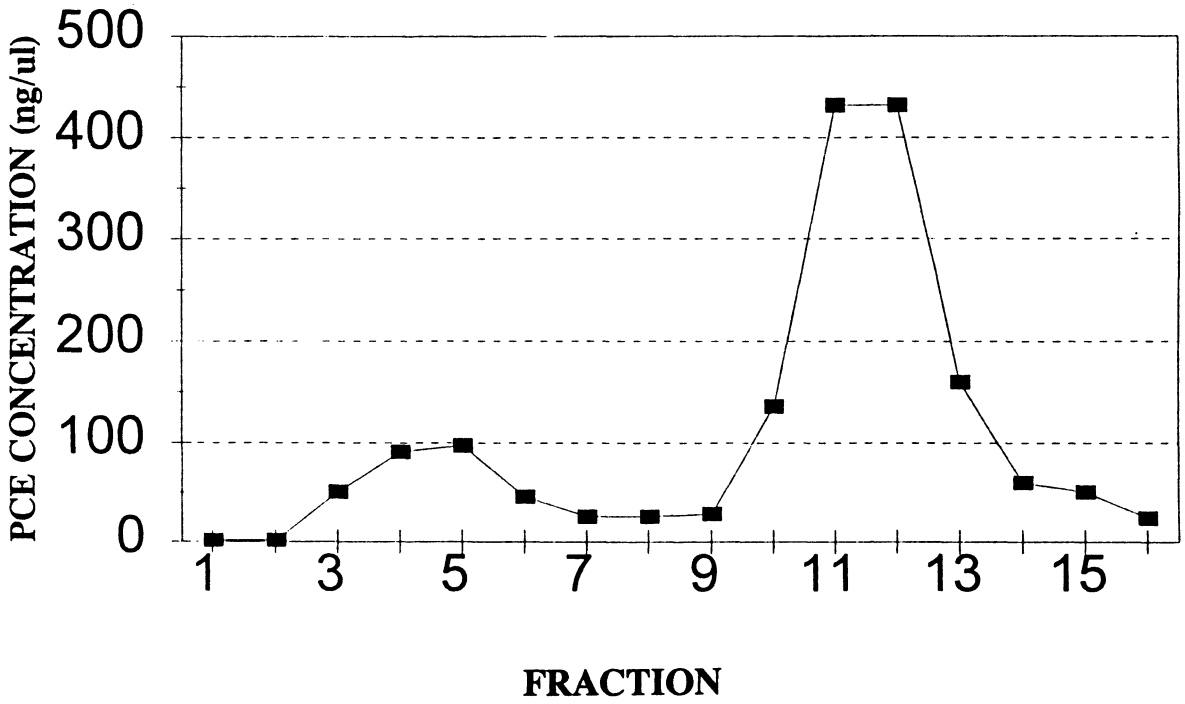

Figure 5-10. Cosolvency Enhancement Curve with Acetone - Trial #2.

The column was emptied and re-packed with a new slurry of the same soil. An additional set of 16 samples was collected as acetone Trial #3 (Table 5-6 and Figure 5-11). Trial #3 was very similar in profile to Trial #1. The maximum pre-cosolvent concentration was in fraction six (126.0 ng/μl) after a slight drop at fraction 5. Also, the maximum post-cosolvent concentration of 854.0 ng/μl appeared early in fraction 10. Cosolvent enhancement between the pre- and post-cosolvent maxima was 6.8. The enhancement between the minimum, fraction 9, and the post-cosolvent maximum was 11.7. These values are indicative of significant cosolvent enhancement with acetone.

Aqueous Ammonia as a Cosolvent

Aqueous ammonia was the third and final cosolvent used in the study. Common household cleaning products contain ammonia and are often disposed of by simply dumping them down the drain. This action could result in significant cosolvent effects without any realization of the consequences. Data has not been found in the literature concerning cosolvency and ammonia; accordingly, it was included in the study. In a newly packed column, the same procedure was followed as was with the acetone trials. Again, it was easy to recognize when ammonia first emerged from the column because of its astringent odor. Ammonia peaks did not appear in the TICs as peaks because the mass spectrometer mass range was set to ignore all m/z ratios below 35; the molecular ion for ammonia is 17.

Table 5-6. PCE Mobility with Acetone as Cosolvent - Trial #3

Fraction	Concentration (ng/μl)
1	5.7
2	4.8
3	63.0
4	114.1
5	73.0
6	126.0
7	124.9
8	88.9
9	73.1
10	854.0
11	137.9
12	35.5
13	13.1
14	5.6
15	3.6
16	3.1

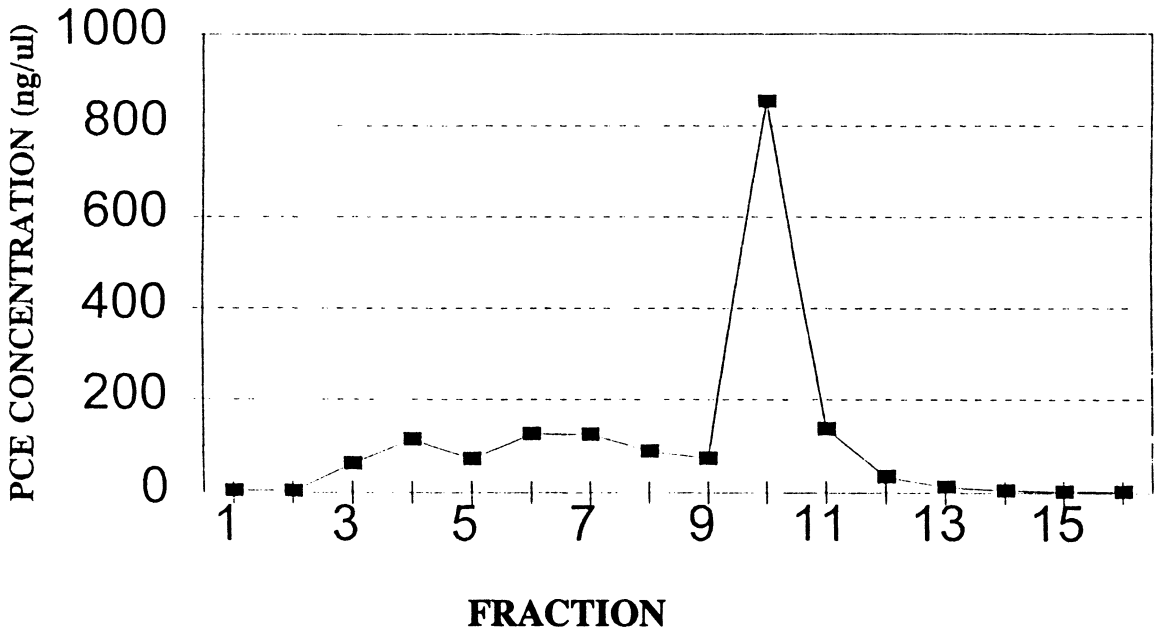

Figure 5-11. Cosolvency Enhancement Curve with Acetone - Trial #3.

Ammonia appears to double the dissolved concentration of PCE under the column flow experimental design. This is evident in the first ammonia trial (Table 5-7 and Figure 5-12). The data reflect the general trends observed for anti-freeze and acetone cosolvents, except that a slightly faster flow rate (about 2.25 ml/min) was employed. Fraction three had the greatest PCE concentration of 114.2 ng/μl with the level systematically decreasing in each subsequent fraction. Upon the injection of cosolvent at fraction nine, a maximum PCE concentration of 230.6 ng/μl was observed, as expected, in fraction eleven. The calculated cosolvency enhancement factor between the two maxima was 2.0. The cosolvency enhancement between fraction 9 and fraction 11 was 14.5.

Without repacking the column, another six milliliters of aqueous ammonia was injected and water was flushed through the system overnight. Then, the established procedure was repeated; Table 5-8 and Figure 5-13 display the results. Again, sample three had the greatest concentration of PCE in the sample (222.1 ng/μl) using the same 2.25 ml/min flow rate as in ammonia Trial #1. The pre-cosolvent maximum is nearly two times higher than that in fraction three of Trial #1. A possible interpretation of this result is that irreversibly sorbed PCE from earlier injections populates a significant number of sorption sites in the column. Because a significant number of sites were already full when the Trial #2 injection of PCE was made, there were fewer sites open to hold the new pulse of PCE.

As usual, fraction 11 contained the maximum PCE concentration after the introduction of cosolvent during collection of fraction 9. This time it was 1097.3 ng/µl,

Table 5-7. PCE Mobility with Aqueous Ammonia as Cosolvent - Trial #1.

Fraction	Concentration (ng/μl)
1	0.0
2	2.0
3	114.2
4	58.7
5	36.8
6	31.2
7	17.8
8	12.0
9	15.9
10	150.0
11	230.6
12	51.1
13	40.6
14	32.7
15	27.3
16	26.8

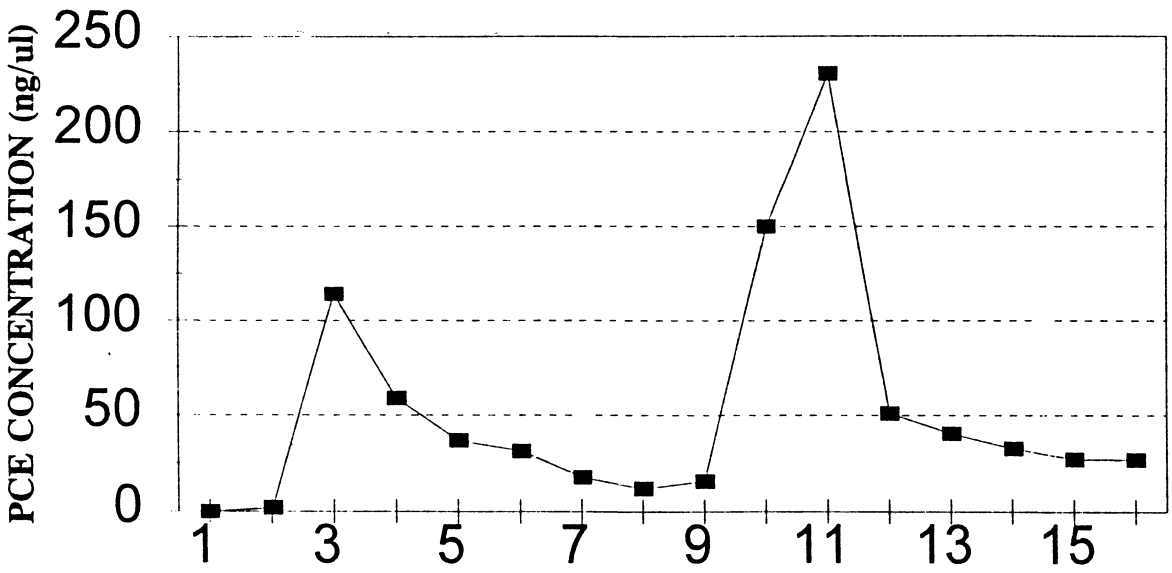

Figure 5-12. Cosolvency Enhancement Curve - Trial #1.

Table 5-8. PCE Mobility with Aqueous Ammonia as Cosolvent - Trial #2.

Fraction	Concentration (ng/μl)
1	0.7
2	4.7
3	222.1
4	130.0
5	113.3
6	104.6
7	67.9
8	52.3
9	55.7
10	462.7
11	1097.3
12	187.4
13	96.7
14	72.3
15	90.4
16	63.7

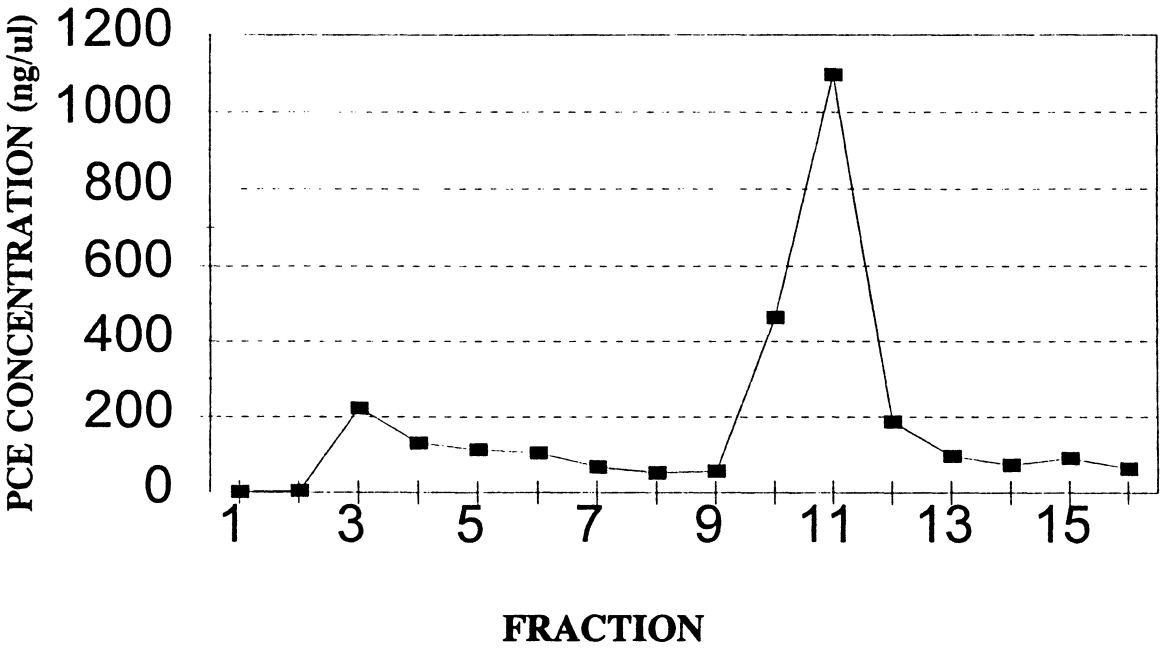

Figure 5-13. Cosolvency Enhancement Curve - Trial #2.

indicating PCE mobility was increased by a factor of 5.0 from the pre-cosolvent maximum. The enhancement between fraction 9 and fraction 11 was 19.7.

The cosolvency of aqueous ammonia was tested a third time after re-packing the column. The flow rate on ammonia Trial #3 was set at 1.5 ml/min. The results compared closely to the third experiment using anti-freeze as the cosolvent, suggesting that channeling might have occurred in the column (Table 5-9 and Figure 5-14). A maximum pre-cosolvent PCE concentration was seen in fraction five (629.4 ng/μl). It began to decline, then increase slightly with fraction nine, and reach a maximum of 530.9 ng/μl in fraction 11. So much PCE cleared the column initially that there was not a significant amount to codissolve with the ammonia. There was no enhancement shown between the pre- and post-cosolvent maxima. The fraction 9 to fraction 11 cosolvent enhancement, however, was 2.61.

Cosolvency Summary

Cosolvency enhancement observed for all nine trials is summarized in Table 5-10. The maximum PCE concentration in the mobile phase after cosolvent injection was divided by the maximum concentration of PCE in the mobile phase before the cosolvent was injected:

$$\text{Cosolvent Enhancement} = \frac{MC_{mix}}{{}^{*}MC_{water}} \qquad \textbf{(5-1)}$$

Table 5-9. PCE Mobility with Aqueous Ammonia as Cosolvent - Trial #3.

Fraction	Concentration (ng/μl)
1	1.2
2	1.6
3	21.5
4	314.8
5	629.4
6	421.3
7	287.7
8	200.4
9	202.7
10	163.4
11	530.9
12	275.5
13	87.7
14	105.2
15	98.9
16	46.3

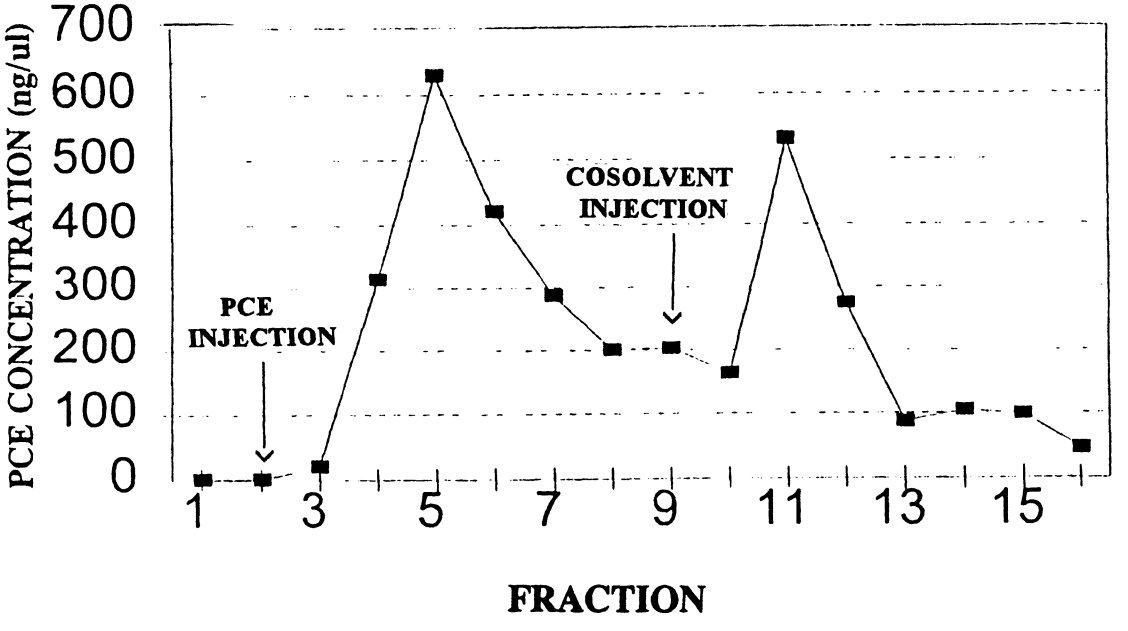

Figure 5-14. Cosolvency Enhancement Curve - Trial #3.

Table 5-10. Cosolvency Enhancement.

Anti-Freeze	Post-Cosolvent Maximum to Pre-Cosolvent Maximum	Post-Cosolvent Maximum to Pre-Cosolvent Minimum
Trial #1	7.26	12.2
Trial #2	9.23	14.6
Trial #3	(channeling)	(channeling)
Average	8.2 (± 1.4)	13.4 (± 1.7)
Acetone		
Trial #1	5.5	7.7
Trial #2	4.6	16.8
Trail #3	6.8	11.7
Average	5.6 (± 1.1)	12.1 (±4.6)
Ammonia		
Trial #1	2.0	14.5
Trial #2	5.0	19.7
Trial #3	(channeling)	(channeling)
Average	3.5 (± 2.1)	17.1 (± 3.8)

where:

MC_{mix} = the maximum concentration of PCE in the mobile phase after introduction of cosolvent.

MC_{water} = the maximum concentration of PCE in the mobile phase before introduction of cosolvent.

*In a second calculation, MC_{water} can also denote the minimum concentration of PCE in the mobile phase before the introduction of the colsolvent.

Cosolvent enhancement between the post-cosolvent maximum and pre-cosolvent maximum was greatest with the anti-freeze mix, even though it was only a 50% ethylene glycol solution. PCE concentration was magnified by an average of 8.25 ($\pm$ 1.4). Neat acetone enhanced the PCE concentration by an average of 5.6 ($\pm$ 1.1) and concentrated ammonia reagent showed the least cosolvent effect on PCE with an average enhancement of 3.5 ($\pm$ 2.1).

Cosolvent enhancement did not follow the same order when measured as the ratio between the post-cosolvent maximum and the pre-cosolvent minimum. Cosolvent enhancement was greatest with the aqueous ammonia 17.1 ($\pm$ 3.8). Anti-freeze enhancement (13.4) and acetone enhancement (12.1) were fairly close.

CHAPTER 6

CONCLUSION

As stated in the opening chapter, ground water contamination in the Missoula Valley became a concern when elevated levels of chlorinated organic compounds were detected in Mountain Water Company wells that supply drinking water. This is a problem that can be compounded by the presence of polar solvents such as anti-freeze, acetone, and aqueous ammonia. Because of their abundance and typical use in industry and households, resolving the quandary about halogenated solvents is not just confined to the Missoula area; but, every community - especially those that rely on an aquifer for their water supply.

The results of this preliminary study demonstrate that cosolvency is an important factor to consider when determining the environmental fate and transport of PCE and other chlorinated organic compounds. Anti-freeze, acetone, and aqueous ammonia each increased transitory PCE concentrations more than an order of magnitude. Aqueous ammonia showed the most dramatic enhancement (17.1) while acetone and anti-freeze exhibited enhancements of 12.1 and 13.4, respectively. To better understand the results from the aqueous ammonia, there may be a need to consider electrostatic interactions and exchange reactions within the experimental set-up ***(5)***. Surprisingly, acetone had the lowest cosolvency effectiveness. The most likely explanation for this result resides in how acetone affects the surface tension and viscosity of the cosolvent system. The lower viscosity of the eluent phase was evident in the need to readjust the column flow

restrictors; the acetone trial had a tendency to run faster for a given hydraulic head. While acetone possessed the greatest estimated equilibrium cosolvent effectiveness in a pyrene study ***(5),*** the dynamics of column flow experiments suggest the eluent moves too quickly to desorb as much as the other cosolvents.

Cosolvency leads to significantly higher quantities of transported PCE than would be found in a straight aqueous system. Taking advantage of the chromatographic character of the cosolvency enhancement plots, one can compute the relative quantities of PCE transported before and after cosolvent injection using the Trapezoidal Rule from the numerical methods literature ***(21):***

$$\textbf{Area} = 0.5 * \Delta x * (0.5y_1 + y_2 + y_3 + \ldots + y_{n-1} + 0.5y_n) \quad \textbf{(6-1)}$$

where Δx is the spacing interval between two fractions, and the y's are the concentrations measured for each fraction. The pre-cosolvent areas are compiled from fractions 2-9; the post-cosolvent areas are compiled from fractions 9-16. The results are presented in Table 6-1 and demonstrate that simple advection considerations will seriously under-estimate PCE mobility when cosolvents are present. The quantified cosolvent enhancement was greatest for the anti-freeze mix with a magnification of 6.4 ($\pm$ .50). Aqueous ammonia was next with an enhancement of 2.5 ($\pm$ .64) and acetone with the lowest enhancement was 1.8 ($\pm$ 1.4). After surmising the area under the peaks of each graph, (Chapter 5, pp. 58-74) it was estimated that the anti-freeze mix would show the greatest cosolvent enhancement. The Trapezoidal Rule calculation confirmed this prediction.

Table 6-1. Relative Transport Quantities of PCE.

	ANTI-FREEZE	ACETONE	AQUEOUS AMMONIA
TRIAL #1			
Fractions 2-9 (ng/μl)	156.2	645.9	279.7
Fractions 9-16 (ng/μl)	1039.5	884.8	553.7
Enhancement	**6.7**	**1.4**	**2.0**
TRIAL #2			
Fractions 2-9 (ng/μl)	386.1	175.7	720.4
Fractions 9-16 (ng/μl)	2331.0	648.6	2066.5
Enhancement	**6.0**	**3.4**	**2.9**
TRIAL #3			
Fractions 2-9 (ng/μl)	1660.7	314.4	1977.3
Fractions 9-16 (ng/μl)	1127.6	543.9	1386.1
Enhancement	**(Channeling)**	**.59**	**(Channeling)**
Average	**6.4 ($\pm$.50)**	**1.8 ($\pm$1.4)**	**2.5 ($\pm$.64)**

RECOMMENDATIONS FOR FUTURE STUDIES

Future column cosolvency studies should address how to construct soil columns more representative of the subsurface. The sieving and slurry procedures used in this study were not entirely satisfactory. Channeling, which was not visible apparent, occurred within the column during two of the nine trials. While channeling was not desired in this study, it could not be neglected because it might realistically occur in the natural environment.

Additional experiments are needed to more strongly confirm the trends noted in these initial studies. One area that has not been explored is how variations in concentrations of the cosolvent affect dynamic cosolvency, i.e. compare the results of a 50/50 anti-freeze injection mix to a 100 percent anti-freeze injection mix.

Due to problems encountered with all soil samples except Sample #3, only one type of soil has been tested for cosolvency effects. It would be informative to explore how other soil columns behave, especially if the soils differed in their fraction of organic matter. (Note: Soils with smaller particle sizes are more likely to contain higher amounts of clay-humic complexes.)

Only three common, non-halogenated solvents have been tested in this thesis research -- and all three exhibited strong cosolvent effects. This suggests that it would be prudent to examine other common industrial and household solvents for their cosolvency characteristics.

Ultimately, the utility of column studies to predict fate and transport of halogenated compounds in the subsurface should be evaluated in a field setting. This would require a hydrological trace study to provide data for comparisons with concentration/transport time values computed from the column study parameters.

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